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FIELD SURVEILLANCE AND ENFORCEMENT GUIDE FOR PETROLEUM REFINERIES

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The report entitled "Field Surveillance and Enforcement Guide for Petroleum Refineries" describes petroleum refining and natural gas processing, refinery equipment, process instrumentation, air pollution monitoring instrumentation, maintenance of refinery records for use by air pollution control personnel, estimating and assessing emissions, plant and equipment maintenance and the qualifications and training requirements of field enforcement personnel. The guide was prepared to familiarize state and local air pollution control officials with the operation of petroleum refineries and natural gas processing plants and to aid agency personnel in developing surveillance, inspection, monitoring, reporting and enforcement procedures.

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Natural Gas	Sulfur Oxides	Natural Gas Processing	
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FIELD SURVEILLANCE AND ENFORCEMENT GUIDE FOR PETROLEUM REFINERIES

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ABSTRACT

A field surveillance and enforcement guide was prepared for use by air pollution control officers in petroleum refineries and natural gas processing plants. The processing facilities used by the petroleum and natural gas industries are described and air pollution sources are identified. The guide includes methods for estimating emission rates and describes instruments for monitoring air pollution sources. Procedures for inspection and surveillance of refineries are presented. Qualification requirements for the field enforcement officers are discussed.

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SUMMARY

This Field Surveillance and Enforcement Guide was prepared to familiarize state and local air pollution control officials with the operation of petroleum refineries and natural gas processing plants and to aid agency personnel developing surveillance, inspection, monitoring, reporting, and enforcement procedures.

The Guide is divided into eight chapters. The first three describe present-day refinery equipment and operation with emphasis on air pollution sources. The remaining chapters describe monitoring equipment, record-keeping requirements and enforcement programs and procedures. A glossary of petroleum industry terms is given at the end of the guide.

CHAPTER I - PETROLEUM REFINING AND NATURAL GAS PROCESSING

A typical refinery consists of a crude distillation unit and a variety of units designed to separate, react, and blend petroleum fractions. Several air pollution sources are common to many refinery process units. Sour water streams contain dissolved sulfur compounds

and ammonia. Fuel gases containing hydrogen sulfide are produced at various locations. Heaters are widely used and produce combustion products such as sulfur oxides, nitrogen oxides, and particulates.

Special air pollution problems associated with specific operations are discussed. These include sulfur oxide emissions from sulfur plants, particulates, carbon monoxide and sulfur oxides from catalytic crackers and catalyst regeneration operations, hydrocarbon emissions from storage and loading facilities, and emissions from flares and blowdown systems.

CHAPTER II - REFINERY EQUIPMENT

Individual equipment items located throughout a refinery have characteristic air pollution problems. Each type of process equipment is described with emphasis on air pollution sources. In general, pumps, compressors, heat exchangers, valves and fittings emit air contaminants by leakage. Furnaces and heaters are a source of combustion pollutants. Relief valves are designed to release gases at certain pressures and represent an important potential source of air pollution.

CHAPTER III - INSTRUMENTATION

Process instrumentation and control equipment, including devices for measuring pressures, temperature, liquid levels, and flow rates, are described. The application of commonly used process instruments to the detection and measurement of air pollution is discussed. A table showing the derivation of the codes for instruments and controls is included.

CHAPTER IV - MONITORING INSTRUMENTATION

Equipment and strategy for monitoring air pollution sources are discussed. Sampling and source monitoring on a local and continuous basis is described. Instruments for determination of sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, and particulates are commercially available. Instruments may be required for monitoring ambient air quality at locations wherewidespread leakage occurs, such as hydrocarbon emissions from valves, pumps, compressors, etc. Use of portable instruments is discussed.

CHAPTER V - MAINTENANCE OF REFINERY RECORDS FOR USE BY AIR POLLUTION CONTROL FIELD ENFORCEMENT OFFICERS

The importance of record keeping in refinery surveillance and control activities is emphasized. Records available from the refiner are described. Records should be kept on emission rates, source registration, permits to operate, complaints, episode histories, and compliance plans. Programs, strategies, and formats for record keeping are described.

CHAPTER VI - ESTIMATING AND ASSESSING EMISSIONS

The procedures for inspection and surveillance of refineries include the initial survey, physical inspection, and follow-up surveys.

The initial survey consists of environmental and external observations including visible emissions, odor detection, and management interviews. The physical inspection includes on-site review of records, sensory tests, instrument readings, equipment inventories and effluent sampling. A resurvey is required to update inspection data and review maintenance records. Techniques for estimating loss rates are discussed.

CHAPTER VII - MAINTENANCE

Refinery maintenance is an important element of refinery operations. Maintenance operations are a source of air pollution, and maintenance records are a valuable source of information to the control officer. Chapter VII describes typical maintenance operations. Maintenance of air pollution equipment and monitoring instruments is discussed.

CHAPTER VIII - PERSONNEL

Manpower requirements for state and local air pollution control agencies depend upon the number and complexity of refineries and other chemical process related plants in the jurisdiction. The function of the field enforcement officer to survey, inspect, and investigate is defined. Personnel qualifications and a list of programs for training and recruiting are given.

INTRODUCTION

PURPOSE

This Guide was prepared to aid state and local air pollution control officials in carrying out effective surveillance and control of air pollution sources in petroleum refineries and natural gas processing plants. The Guide is designed to familiarize control officials and field enforcement officers with the operation of petroleum refineries and natural gas processing plants. In the description of refinery equipment operations, particular emphasis is given to the air pollution aspects. Another important purpose is to provide guidance to agency personnel in developing surveillance, inspection, monitoring, reporting and enforcement procedures.

SOURCES OF INFORMATION

Private and public sources were used to prepare the Guide. Public sources include textbooks and journals which are widely distributed in the petroleum industry. Some general references are listed at the end of this Introduction. Manufacturers and suppliers were relied upon for information on equipment and monitoring instrumentation. Catalogs of air pollution control equipment suppliers are regularly published by Chemical Engineering and Environmental Science and Technology. The files of The Ben Holt Co. and Pacific Environmental Services, Inc. were also sources of information.

ROLE OF REFINERIES IN THE PETROLEUM INDUSTRY

The petroleum industry is divided into the following functional operations: exploration, production, transportation, marketing and distribution, and refining. An oil company may perform only one or a few or all of these functions. Exploration and production companies search for oil and gas reserves, drill wells, and develop and produce the resource. Many companies provide only transportation services - using pipeline, barge, rail, tanker, and truck facilities. Marketing and distribution generally refers to petroleum products only. This function includes sales, advertising, and distribution to retail and commercial outlets.

The refining function includes a broad range of processing and manufacturing operations designed to convert crude oil and natural gas to saleable products. In the early days of the oil industry, the refining function consisted only of batch distilling of crude oil. As the number and quality of petroleum products increased, a myriad of refining processes were developed to effect both chemical and physical changes in petroleum. Today, there are literally hundreds of these processes available. Each refinery consists of a combination of them. The configuration of each refinery and natural gas processing plant depends on the feed stock and product specifications. Field enforcement officers should not expect to find all or even a majority of the process equipment and abatement techniques presented (in Chapters I and II). Many factors, such as throughput, geography, and slate and product split, affect not only the number and types of processes utilized, but also the abatement controls necessary. By understanding the function and operation of each refinery process, the field enforcement officer will gain the knowledge of the refining industry necessary to the effective performance of his tasks.

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JOURNALS

Chemical Engineering
Environmental Science and Technology
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Journal of the Air Pollution Control Association
Oil and Gas Journal

I. PETROLEUM REFINING AND NATURAL GAS PROCESSING

A. INTRODUCTION

Crude petroleum is a mixture of hydrocarbons and small amounts of sulfur, nitrogen, oxygen, and various metals. Crude oils are classified as being derived from paraffinic, naphthenic, or intermediate base stocks. The characteristics of a given crude can vary from a clear liquid in the gasoline range to a pitch that is so viscous it must be heated to be pumped. Crudes from geographically related oil fields tend to have similar compositions and properties.

Refineries are designed to convert one or more types of crude oil into saleable petroleum products. The types of oil processed and the products desired determine the facilities of a refinery. Theoretically, it is possible to produce any type of product from any crude oil, but in practice economic considerations usually decide which products will be produced.

The trace elements in petroleum also affect the processing steps and, to some extent, the pollutant emissions from the refinery. A high sulfur content in the crude oil increases the corrosive characteristics of the oil and its products. After processing in the refinery, sulfur tends to concentrate in the light ends and gases in the form of hydrogen sulfide and in the heavy ends as complex sulfur compounds. Generally, the hydrogen sulfide is selectively removed from the process gas by treating with ethanolamines. The hydrogen sulfide is regenerated from the ethanolamines and is usually sent to a sulfur recovery unit. New air pollution control regulations will require removal of hydrogen sulfide and its conversion to sulfur, or the use of some other mechanism for controlling sulfur emissions. The residual fuels which contain high percentages of sulfur can be treated by hydrotreating or hydrocracking processes to reduce the sulfur content of the fuel oil to a level that is acceptable to local air pollution control agencies. The sulfur is converted to hydrogen sulfide and enters the process gas stream.

Trace metals such as iron, nickel and vanadium are present in crude petroleum and act as a poison to some catalysts. As the metal accumulates on the catalyst, the activity of the catalyst decreases. Crudes with high concentrations of metal deposits require more frequent catalyst regeneration and replacement. These operations generally release pollutants to the atmosphere and should be carefully controlled.

The products from a refinery vary widely with location, climate and time of year. In winter, there is a high demand for heating fuel oils, and the gasoline products must contain a high percentage of volatile components for cold weather starts. In summer, the demand for fuel oil declines, the demand for gasoline increases, and the volatility of the gasoline must be reduced to minimize vaporization losses and carburetor vapor lock. Refineries must be sufficiently flexible to meet these varying demands.

Table 1 shows the type of products that might be prepared at three typical refineries that differ in size, location and climate.

Table 1. PRODUCTS FROM THREE TYPICAL REFINERIES

Products	Refinery 1[a]	Refinery 2[b]	Refinery 3[c]
Feed, bbl/day	10,000	80,000	200,000
LPG	x	x	x
Olefins			x
Gasoline	x	x	x
Jet Fuel		x	x
Kerosene	x	x	x
Diesel		x	x
Fuel Oil	x	x	x
Heavy Fuel Oil	x	x	x
Naphthenates			x
Solvents		x	x
Asphalt		x	x
Lubricating Oils			x
Greases			x
Petroleum Coke			x

a. Refinery 1 is assumed to have a crude capacity of 10,000 bbl/day.
b. Refinery 2 is assumed to have a capacity of 80,000 bbl/day.
c. Refinery 3 is assumed to have a capacity of 200,000 bbl/day.

As the size of the refinery increases, the number of products increases and the processing operation becomes more flexible. The production rate of each of the products shown can be varied significantly by making relatively minor changes in refinery processing conditions. Hydrocarbon fractions can be shifted from one product to another to meet product demands.

Figure 1 is a flow diagram of a low-capacity, basic refinery which contains only the minimum number of elements to supply a local area with fuels. This type of refinery is relatively inflexible and produces only a limited number of products.

Figure 2 is a flow diagram of an intermediate capacity refinery. This facility has more processing units and a much wider range of products. These diagrams show only the most fundamental processing operations. A large, complex refinery would be about the same with the addition of specialty processes.

Operations such as sweetening, hydrotreating, hydrocracking, sour-water treatment, and sulfur plants are now needed for pollution control in most refineries. They are not shown because they do not affect the principal product streams, but they are essential in modern refinery practice and will be found in every modern refinery.

Many refinery products, for which a special but limited market exists, are manufactured by only a few refineries. In this category are:

Asphalt
Benzene
Cresols
Detergents
Greases
Lubricating Oil
Naphthenic Acid
Aliphatic Solvents
Petroleum Coke
Petroleum Solvents
Phthalic Anhydride
Tar
Toluene
White Gasoline
Xylene

The FEO should expect to encounter at least a few of them.

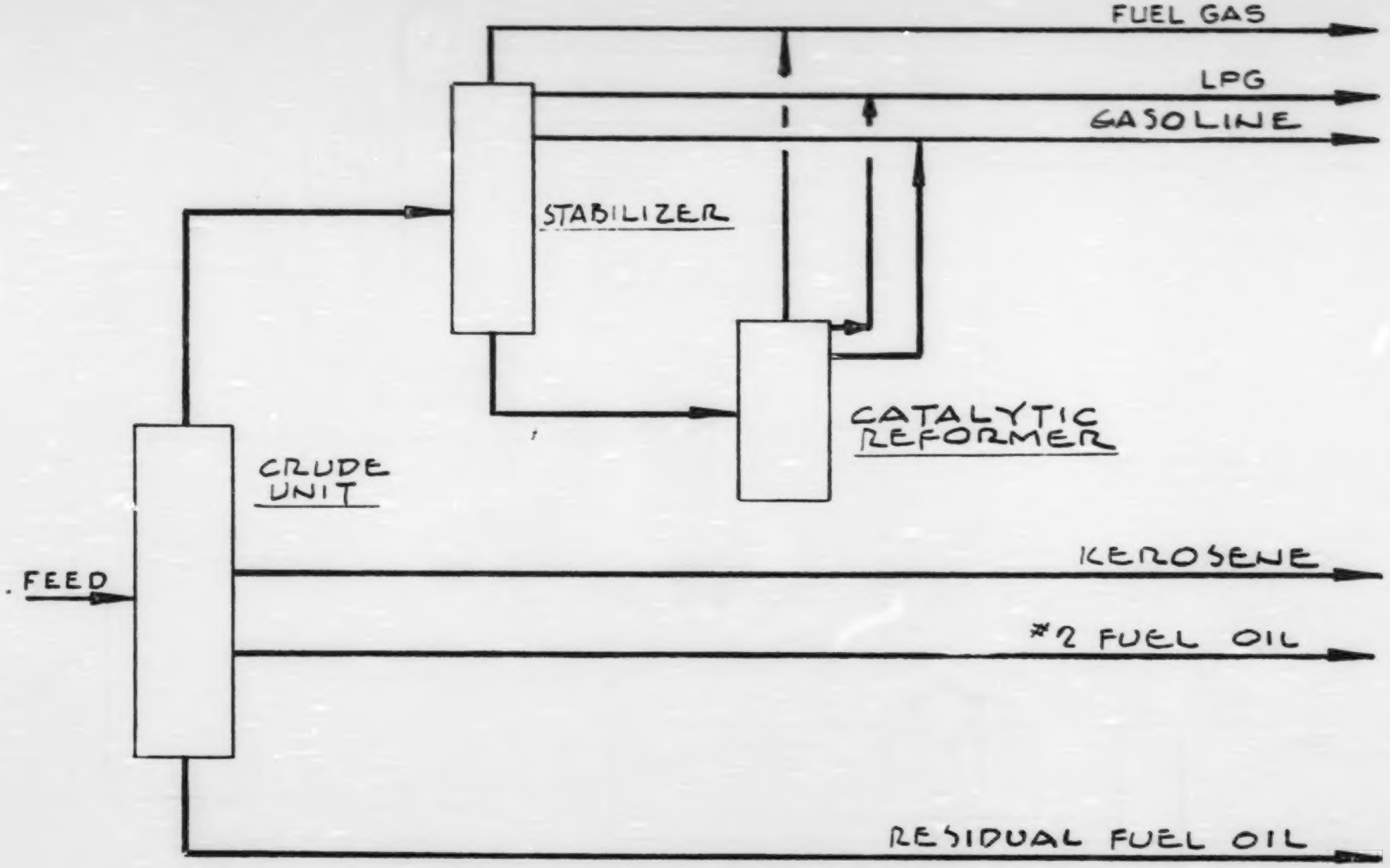

FUEL GAS
LPG
GASOLINE
STABILIZER
CATALYTIC REFORMER
CRUDE UNIT
FEED
KEROSENE
#2 FUEL OIL
RESIDUAL FUEL OIL

Figure 1. Flow diagram of a small oil refinery.

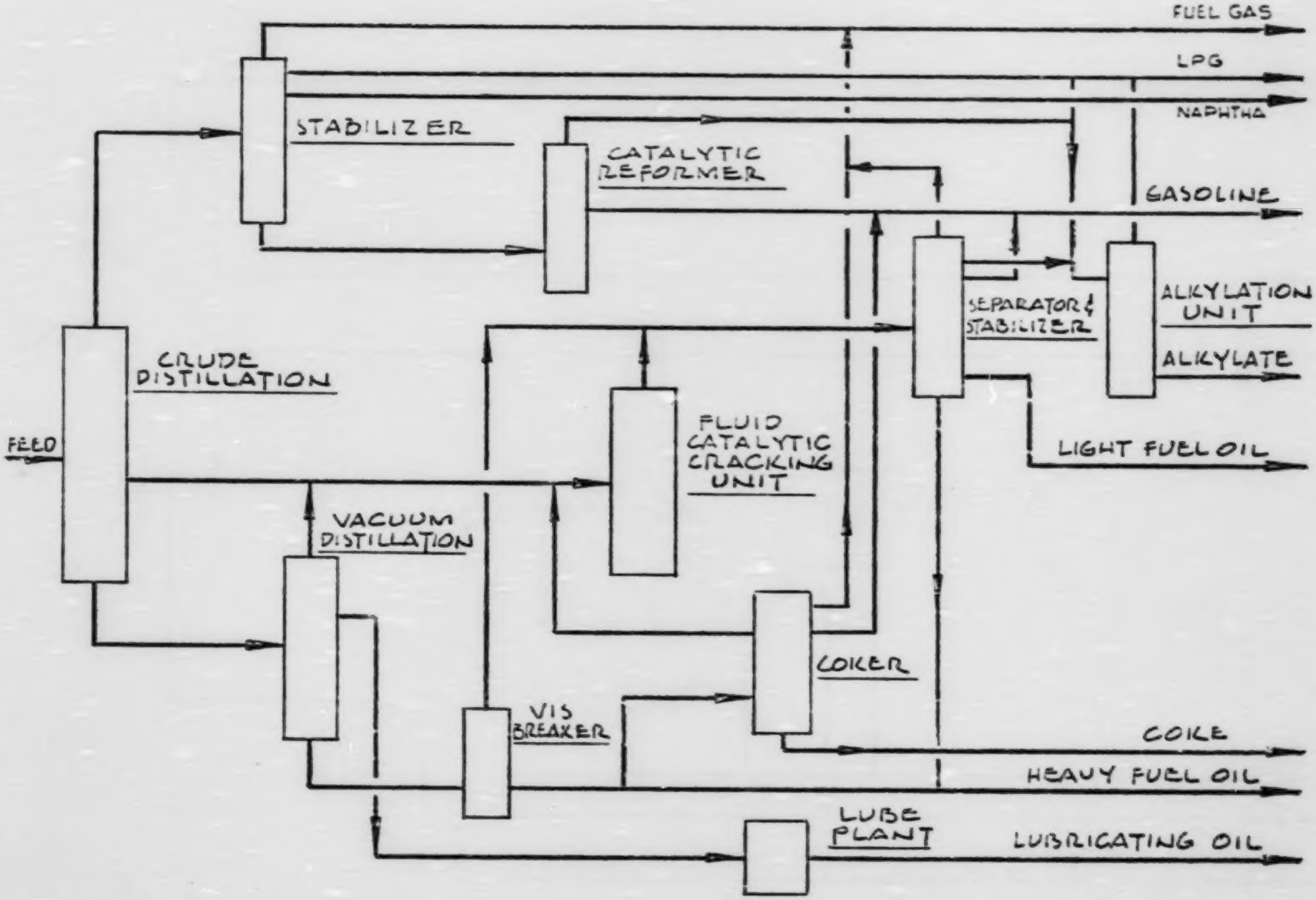

FUEL GAS
LPG
NAPHTHA
STABILIZER
CATALYTIC REFORMER
GASOLINE
SEPARATOR & STABILIZER
ALKYLATION UNIT
ALKYLATE
CRUDE DISTILLATION
FEED
FLUID CATALYTIC CRACKING UNIT
LIGHT FUEL OIL
VACUUM DISTILLATION
COKER
VIS BREAKER
COKE
HEAVY FUEL OIL
LUBE PLANT
LUBRICATING OIL

Figure 2. Flow diagram of an intermediate oil refinery.

Refineries may be divided into on-site facilities and off-site facilities. On-site facilities consist of the petroleum processing units. Off-site units are made up of the support facilities which include wastewater treatment, power generation, steam plant, water treatment, and feed and product storage. Both on-site and off-site processing units are discussed in detail in this chapter. Flow diagrams illustrate the processing units. On the diagrams, the point sources of pollution discussed in the text are indicated by numbered diamonds -- ⟨1⟩, ⟨2⟩, etc. The identification codes used in the figures are explained in Table 8 within Chapter III, Process Instrumentation.

B. CRUDE DISTILLATION AND DESALTING

1. Crude Distillation Unit

The crude distillation unit (Figure 3) is the first refinery unit to process the crude oil. The unit separates the incoming crude oil into light naphtha, heavy naphtha, middle distillates, and bottoms residue. The bottoms residue is usually further processed in a vacuum unit to produce heavy gas oils and a vacuum residuum.

The crude oil is pumped from tankage, preheated by exchange with the products to about 250-300° F, and then desalted. Booster pumps, downstream of the desalter, pump the crude oil through additional heat exchange and through a crude furnace. The temperature of the oil coming out of the furnace is usually 650 - 700° F. From the furnace, the crude oil passes to the crude distillation column. Light

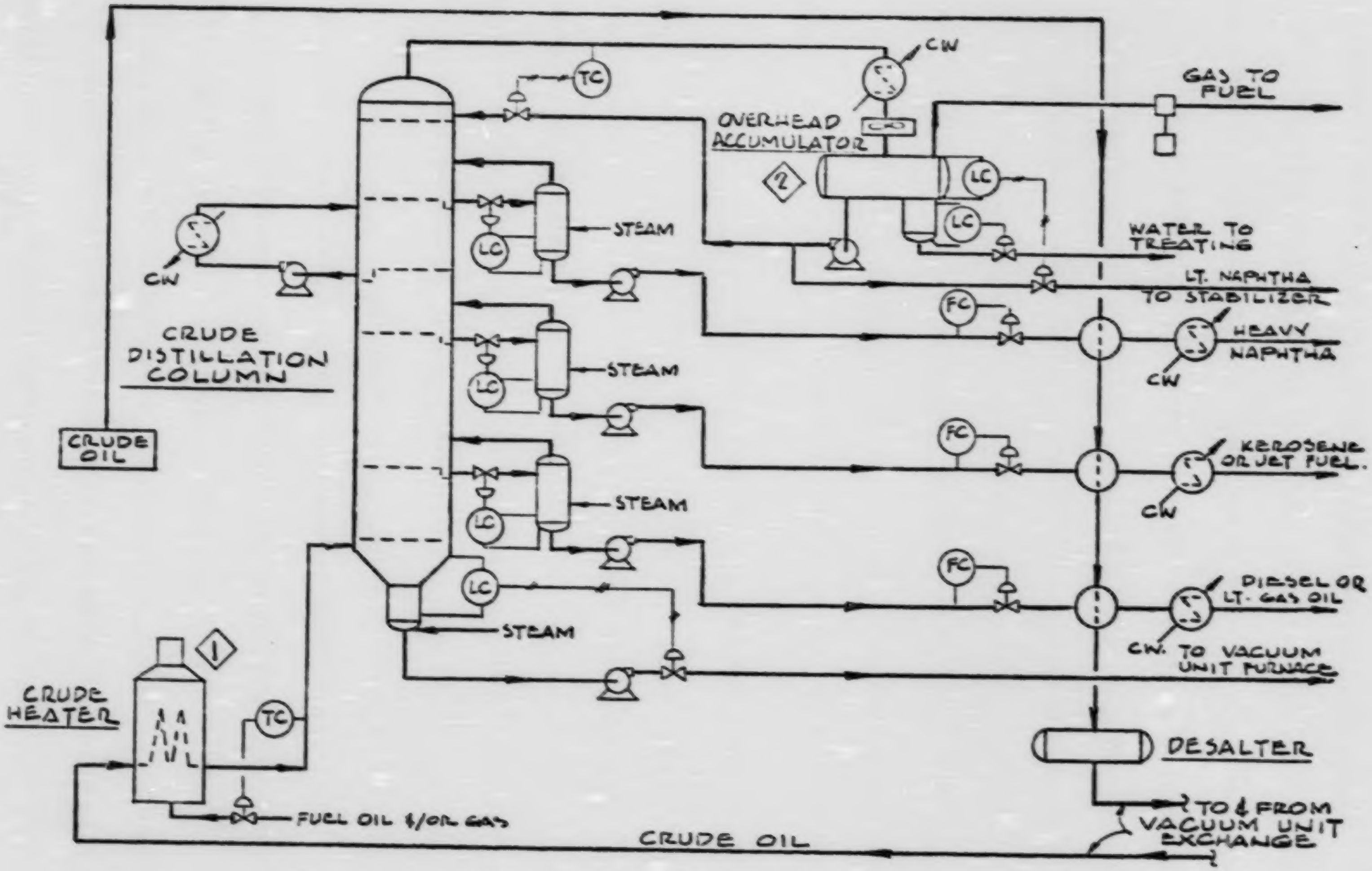

CRUDE OIL
CRUDE DISTILLATION COLUMN
CW
TC
STEAM
STEAM
STEAM
STEAM
LC
LC
LC
LC
CW
OVERHEAD ACCUMULATOR
2
LC
LC
GAS TO FUEL
WATER TO TREATING
LT. NAPHTHA TO STABILIZER
FC
FC
FC
HEAVY NAPHTHA
CW
KEROSENE OR JET FUEL.
CW
DIESEL OR LT. GAS OIL
CW.
TO VACUUM UNIT FURNACE
DESALTER
TO & FROM VACUUM UNIT EXCHANGE
1
CRUDE HEATER
TC
FUEL OIL &/OR GAS
CRUDE OIL

Figure 3. Crude distillation unit.

naphtha and reflux are condensed in the overhead condenser. Water remaining in the crude and entering the tower from the stripping steam is also condensed overhead. The foregoing products plus any noncondensed gases pass to the overhead accumulator where the phases are separated. Gas may be compressed to the fuel gas system or for light hydrocarbon recovery. In some instances, it may be vented to the flare system. The light naphtha is pumped to the stabilizer. The reflux is pumped back to the crude tower for control of the overhead temperature. The water is pumped off plot for treating.

The crude tower usually produces three or more sidestreams which are stripped of their light ends by the use of steam in a sidestream stripper tower. Each sidestream (usually heavy naphtha, kerosene, and gas oil) is heat exchanged with crude oil, cooled in a water or air-cooled exchanger, and pumped to storage.

The hot residual is steam stripped in the base of the crude tower and then, in most refineries, it is pumped directly to a vacuum unit heater. Alternatively, the hot residual oil may be cooled by exchange with the incoming crude oil and with cooling water before being pumped to storage.

The point sources of pollution in the crude distillation unit are the crude heater (point 1 on the figure), the overhead accumulator vent (point 2), water from the overhead accumulator, and the stream sample connections.

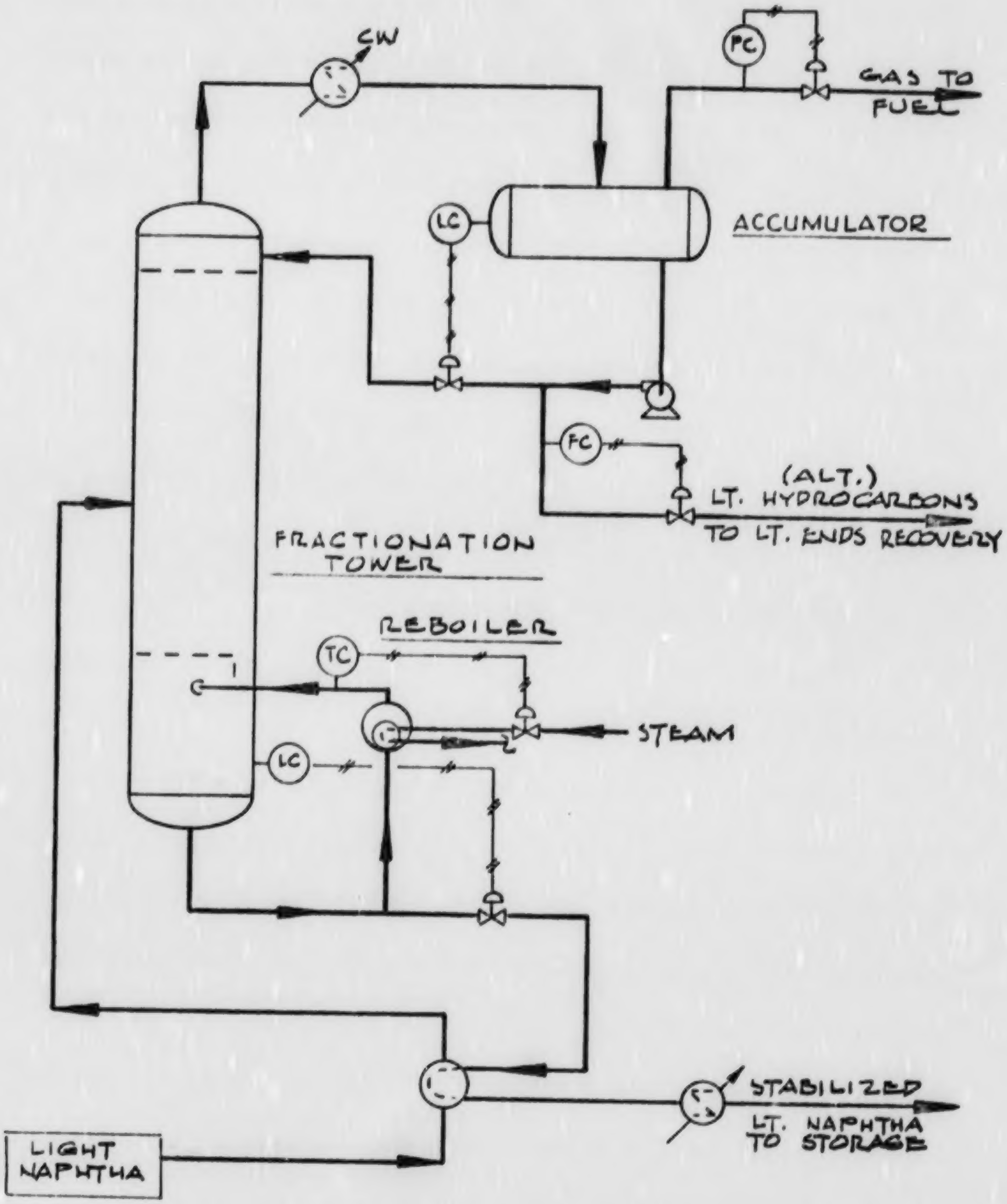

CW
PC
GAS TO FUEL
LC
ACCUMULATOR
FC
(ALT.) LT. HYDROCARBONS TO LT. ENDS RECOVERY
FRACTIONATION TOWER
REBOILER
TC
STEAM
LC
STABILIZED LT. NAPHTHA TO STORAGE
LIGHT NAPHTHA

Figure 4. Naphtha stabilizer.

2. Naphtha Stabilizer

Light naphtha from the crude unit is preheated by exchange with the stabilized naphtha and sent to the stabilizer (Figure 4). This is usually a 20 to 30-tray tower in which only mild fractionation (essentially stripping) takes place. The light gases are removed overhead in the tower in order to reduce naphtha vapor pressure. The naphtha may then be used as a JP-4 jet fuel or gasoline component. Reflux is condensed overhead and the gas is usually sent directly to fuel gas through a back pressure controller. Alternatively some liquid may be produced overhead in a high-pressure light ends recovery unit. The stabilizer bottoms are reboiled by means of a steam heated reboiler. The stabilized light naphtha is sent to storage after suitable cooling in an exchanger and water cooler.

3. Crude Desalter

Desalters are not always required, but when used are the first unit operation applied to the crude. The crude oil passes through the desalter to remove salt, silt, sand, water, and other crude oil contaminants (Figure 5). Water and sometimes demulsifying chemical are added to the crude oil stream usually before preheating. The mixture is passed through an electrostatic field inside the drum after preheating by exchange to 250 - 300° F. The desalter can usually be blocked in, bypassed, and drained during normal operation. A point source of pollution is the desalter water effluent (point 1 in the figure) which will contain a mixture of oil, water and chemicals.

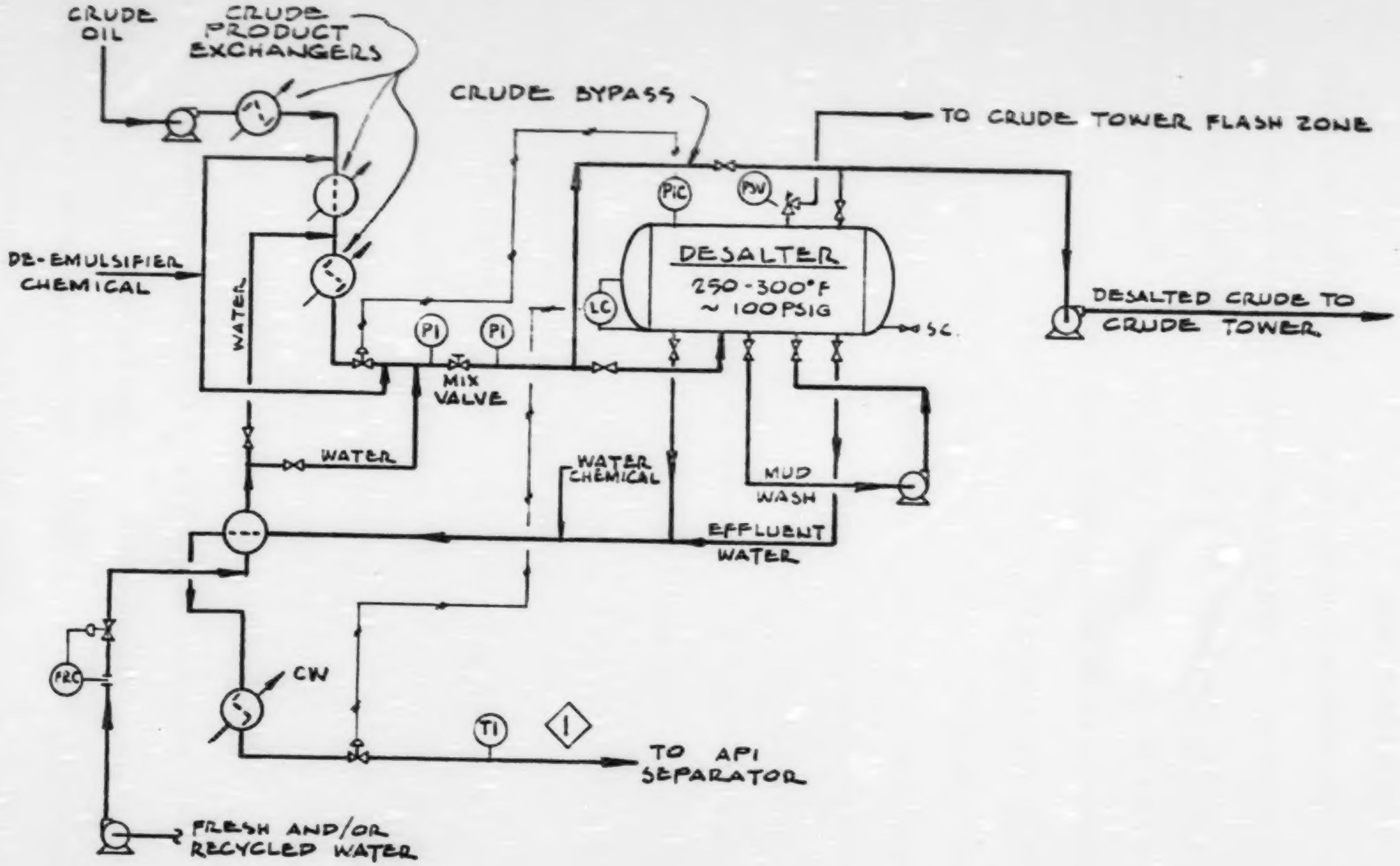

CRUDE OIL
CRUDE PRODUCT EXCHANGERS
CRUDE BYPASS
TO CRUDE TOWER FLASH ZONE
DE-EMULSIFIER CHEMICAL
WATER
PIC
PSV
DESALTER
250-300°F
~ 100 PSIG
LC
PI
PI
SC
MIX VALVE
DESALTED CRUDE TO CRUDE TOWER
WATER
WATER CHEMICAL
MUD WASH
EFFLUENT WATER
PRC
CW
TI
1
TO API SEPARATOR
FRESH AND/OR RECYCLED WATER

Figure 5. Crude desalter.

The sour water effluent from the desalter often must be processed in a sour water stripper or oxidizer for purification. Sometimes this water is degassed and then recycled back to the crude oil. The gas must be treated for H_2S removal and is a possible point source of pollution. The desalter is usually equipped with these sampling connections: oil-water emulsion (feed), desalted oil, desalter internal sampler, and effluent water sampler.

Sometimes two-stage desalting is employed to further remove salts, etc., from the crude oil. This is merely two desalter drums in series and the point sources of pollution are the same for both vessels.

4. Vacuum Unit

In the vacuum unit, hot residual bottoms from the crude unit enter the vacuum tower by way of a vacuum heater which heats the oil to 700 - 750°F (Figure 6). The process here again is distillation, but this time at a reduced pressure (vacuum). The pressure will usually be 25 - 100 mm Hg absolute (equivalent to 735 - 660 mm Hg vacuum). The combination of higher temperature and lower pressure allows additional distillation to take place.

Any vacuum gas oils are taken off from the side of the vacuum tower, exchanged with feed, cooled in a water-cooled heat exchanger and pumped to storage. A small amount of gas oil plus any noncondensables are taken overhead to the jet ejector system. Normally three to five jet ejectors are employed with intercooling, and aftercooling is provided. The overhead streams are sent to an accumulator where the

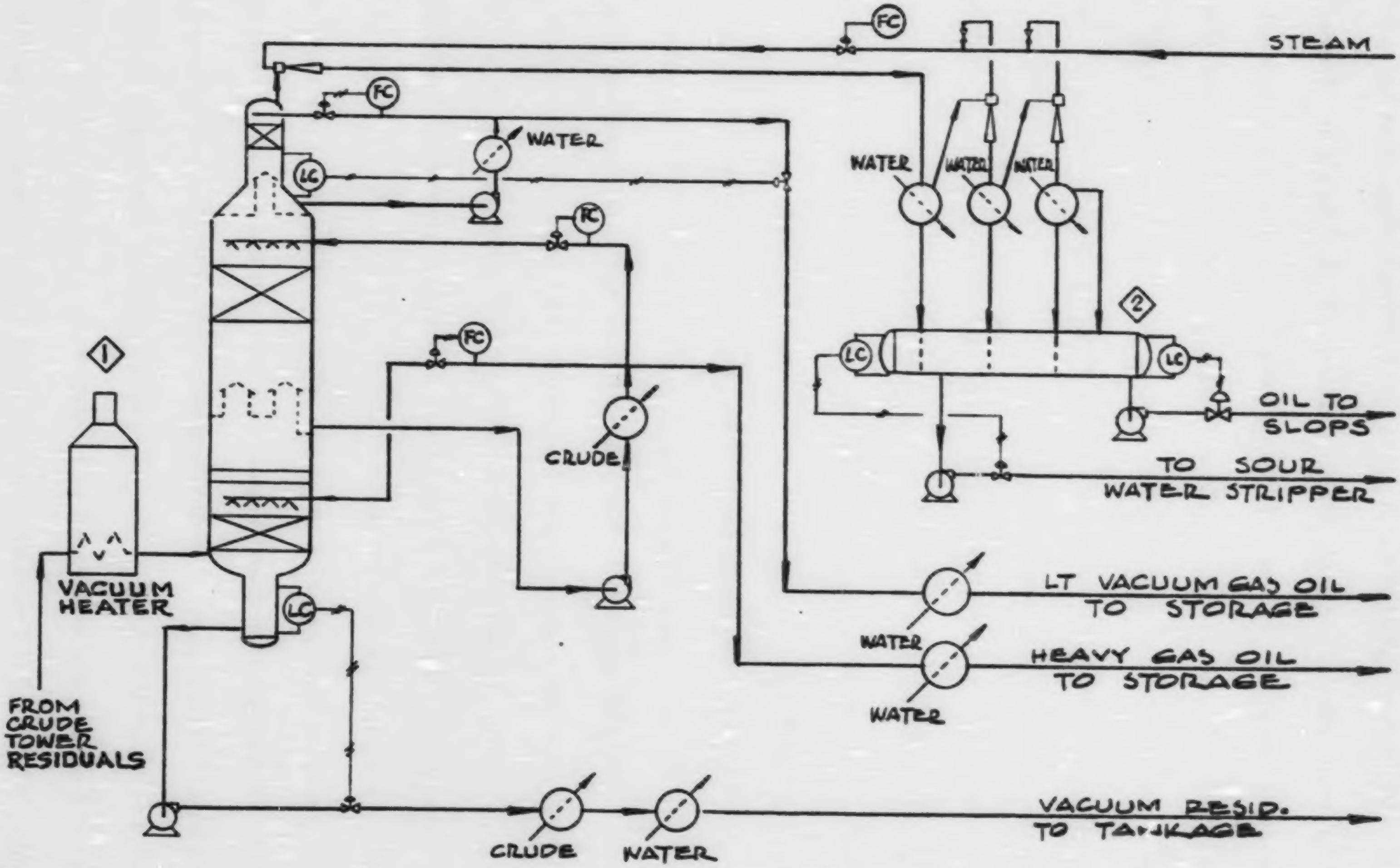

STEAM
FC
FC
WATER
LC
FC
FC
WATER
WATER
WATER
2
LC
LC
OIL TO SLOPS
TO SOUR WATER STRIPPER
1
CRUDE
VACUUM HEATER
LC
LT VACUUM GAS OIL TO STORAGE
WATER
HEAVY GAS OIL TO STORAGE
WATER
FROM CRUDE TOWER RESIDUALS
VACUUM RESID. TO TANKAGE
CRUDE
WATER

Figure 6. Vacuum unit.

phases are separated. Gas is vented to a heater for burning or to a gas recovery unit for purification. The hydrocarbon liquid is usually sent to a slops tank. The water phase is sent to a sour water stripper for purification. The hot vacuum residual is sent either to storage via crude exchange and water cooling or directly to a coking unit.

5. Pollution Sources

The major point sources of air pollution for the crude distillation unit are shown in Figure 3. The crude heater is a fired heater and the stack gas (point 1) contains pollutants (see Chapter II). The overhead accumulator vent (point 2) may contain H_2S and hydrocarbons. Depending on the amount and composition of the vent gas, the gas may be flared or sent to the fuel gas system.

The naphtha stabilizer is a closed system and should have no major point sources of air pollution.

The air pollution point source for the desalter is shown in Figure 5. The water effluent (point 1) may be sour and, if so, it should be sent to a sour water stripper.

Air pollution point sources for the vacuum unit are shown in Figure 6. The vacuum heater is a fired heater and the stack gases (point 1) will contain pollutants (see Chapter II). The overhead accumulator vent (point 2) may contain H_2S and hydrocarbons and should be vented to a heater for burning or should be sent to a gas recovery unit.

C. THERMAL CRACKING

1. Process Objective

Thermal cracking of petroleum is one of the oldest refinery operations and continues to play an important role in many refineries today. Thermal cracking is the process whereby large hydrocarbon molecules are converted into smaller molecules through the process of thermal decomposition. The objectives of the process vary widely depending on the feed stock and the severity of cracking. Cracking feed stocks vary from very light materials such as butane to very heavy vacuum residual tar. Cracking of light hydrocarbon gases and distillates to produce ethylene, propylene and butylene will not be considered here. Olefin plants are commonly considered petrochemical processes even though olefin generation is important in the refinery scheme. Severe cracking of vacuum tars to produce petroleum coke and cracked distillates will be covered in the "Coking" section.

Present day cracking operations can be divided into once-through and recycle plants. In recycle plants, the partially thermally cracked feed is distilled to separate the uncracked portion. Part or all of this uncracked material is then recycled to the cracking section. Visbreaking is a once-through cracking process where a heavy residual fuel oil is mildly cracked to reduce fuel oil viscosity. Recycle thermal cracking plants often involve a variety of cracking and distillation steps to produce a range of petroleum products. The most common recycle cracking plants today feed gas oil and produce a high yield of cracked gasoline. Thermal reformers have been used to convert straight run naphthas to high octane gasoline. Today, however, catalytic reforming is used for this purpose. See Section J, Reforming.

2. Cracking Furnaces

The cracking operation takes place in a tubestill furnace similar to other furnaces in the refinery. Cracking furnaces are designed to control residence time and temperature. Unlike other refinery heaters, cracking furnaces are designed to heat the process stream to temperatures in the 800 to 1100°F range. The furnace consists of radiant and convection sections. Burners located near the floor provide radiant heat to the tubes on furnace walls. Heat is recovered from the combustion gases in the convection section at the top of the furnace. The convection section may be used to preheat air, generate steam, or heat other process streams. Coking of tube surfaces is an important design consideration. The hot tube surface causes coke to deposit on the tubes especially in liquid phase cracking operations. As coke accumulates, heat transfer is impaired and the tube wall temperature rises. Regular cleaning of tube surfaces is required to maintain operating efficiency.

3. Process Description

a. Visbreaking - The process flow diagram for a typical visbreaker is shown in Figure 7. Vacuum residual tar is preheated by heat exchange with visbroken fuel oil and fed to the visbreaker furnace. Mild cracking in furnace tubes produces a

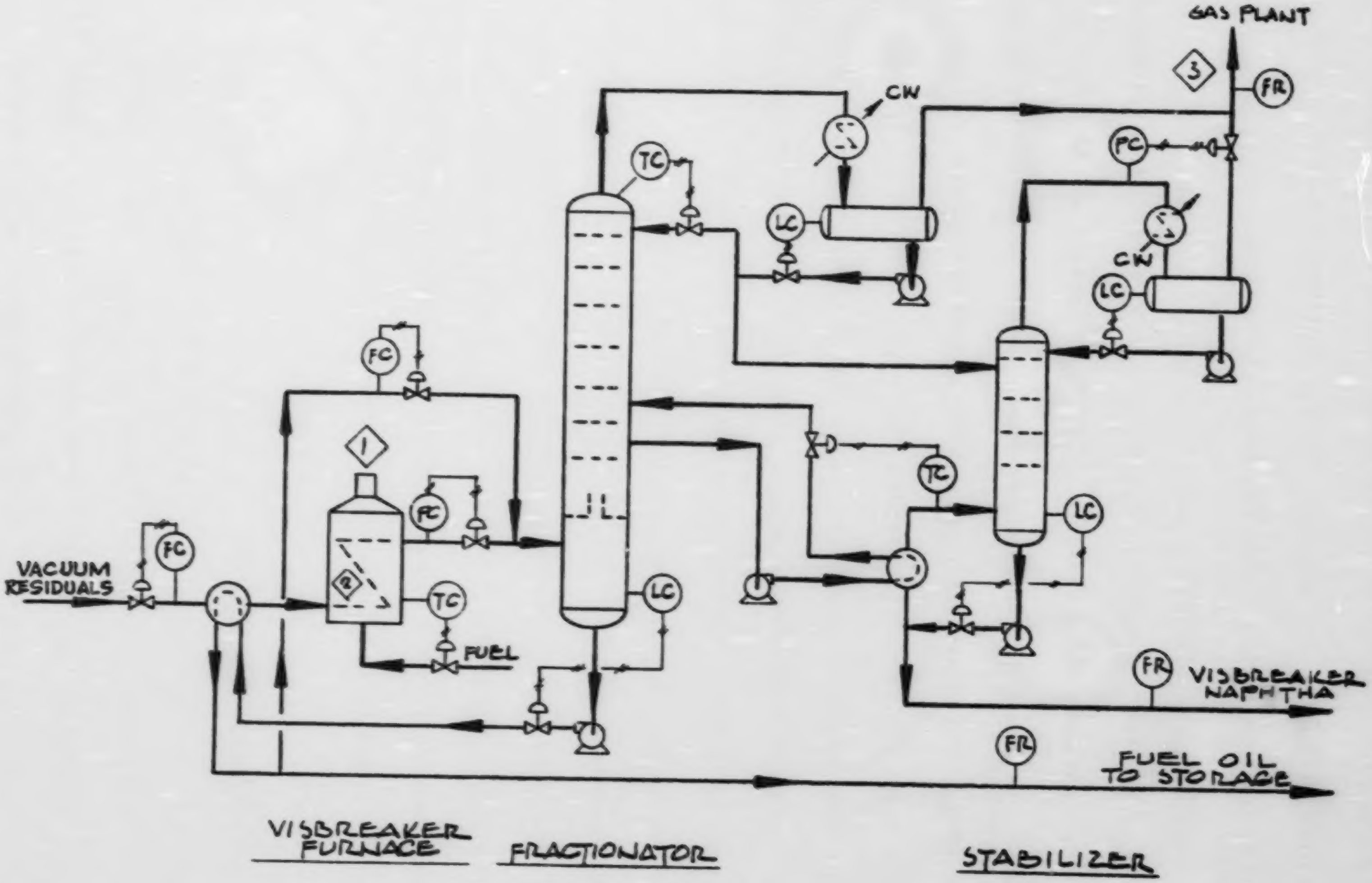

GAS PLANT
3
FR
CW
PC
TC
LC
CW
LC
FC
1
FC
VACUUM RESIDUALS
FC
TC
FUEL
LC
TC
LC
FR
VISBREAKER NAPHTHA
FR
FUEL OIL TO STORAGE
VISBREAKER FURNACE
FRACTIONATOR
STABILIZER

Figure 7. Visbreaker.

mixture of residual oil, naphtha and gas. The reaction products are quenched with a recycle stream and fractionated in a distillation tower. In most visbreakers, no cracked material is recycled to the cracking furnace. The visbroken fuel oil is blended with other components to meet viscosity, sulfur and pour point specifications. Visbreaker naphtha is taken overhead and stripped of light ends in the stabilizer. The naphtha may be desulfurized and reformed before blending into gasoline. Light ends containing hydrogen sulfide are taken from the overhead accumulators on the fractionator and stabilizer. These gases may be processed further in a gas recovery plant or fed directly to the refinery fuel gas system. A side cut is taken off the fractionator to provide internal cooling and heat for the stabilizer reboiler.

b. Thermal Cracking - The process flow diagram for a typical thermal cracking process with a single recycle stream is shown in Figure 8. The feed stock in most units is a reduced crude. The feed is preheated by exchanging with other process streams and charged to the quench tower. The feed serves to quench the furnace discharge to about 800 to 850°F. The quench tower separates residual fuel oil from distillate petroleum. In this scheme, none of the residual material (black oil) is cracked thus reducing coke buildup in the furnace. The quench tower contains several bubble trays to ensure an

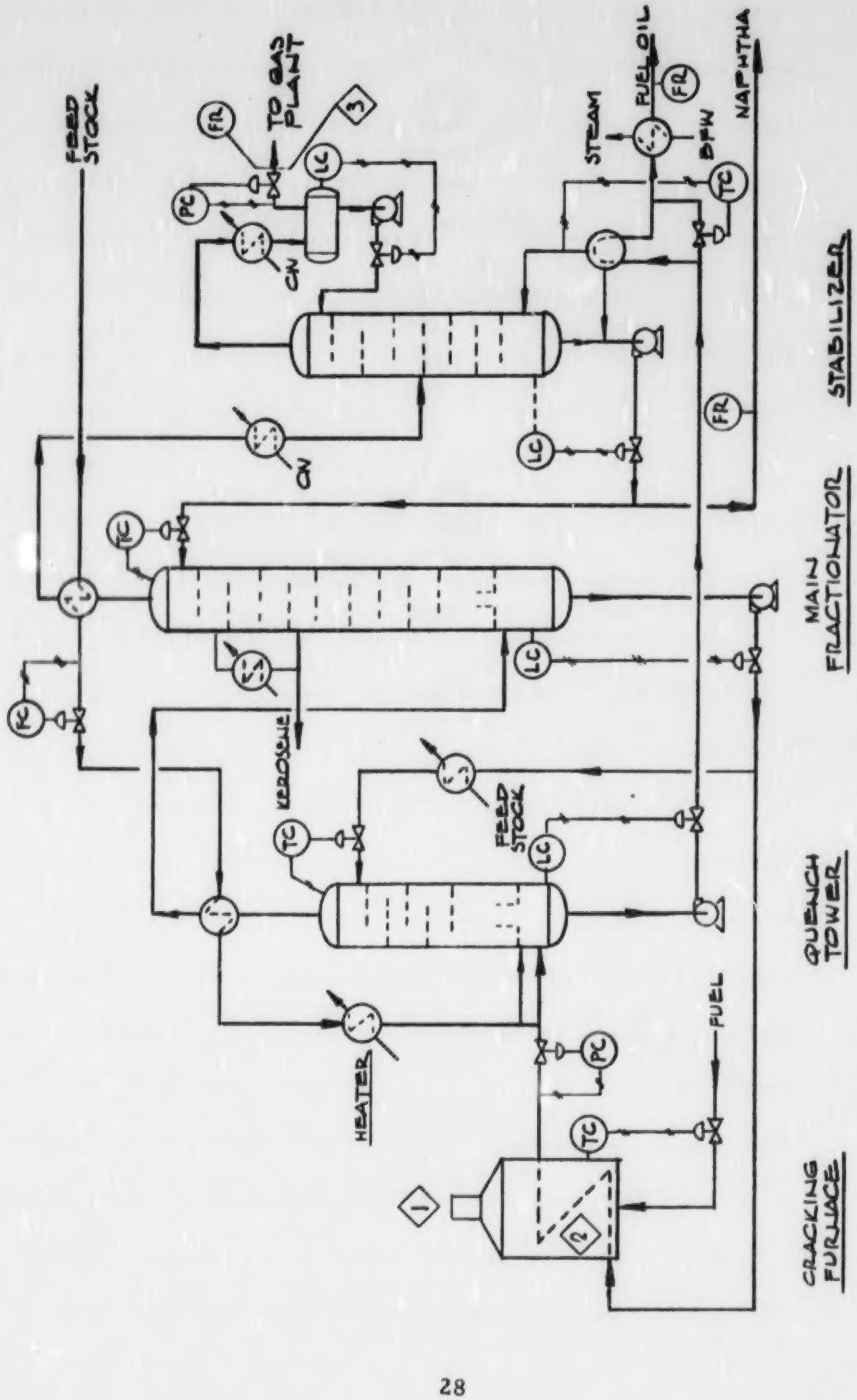

CRACKING FURNACE
QUENCH TOWER
MAIN FRACTIONATOR
STABILIZER
HEATER
FUEL
FEED STOCK
FEED STOCK
KEROSENE
TO GAS PLANT
STEAM
FUEL OIL
BFW
NAPHTHA
CW
CW
PC
PC
PC
TC
TC
TC
TC
LC
LC
LC
LC
FR
FR
FR
1
2
3

Figure 8. Thermal cracking unit.

efficient separation of residual oil. The overhead vapors, containing straight run and cracked distillate are separated in the fractionator. The heavy gas oil from the bottom of the fractionator is fed to the cracking furnace which is operated at elevated pressure. The pressure at the furnace outlet is dropped sharply to the quench tower pressure. One or more side cuts are taken off the fractionator. The overhead vapors containing naphtha are separated in a stabilizer similar to the one used in a visbreaker.

Most thermal cracking plants are combination plants containing two or more cracking furnaces. Side cuts from the main fractionator are recycled to separate furnaces to provide selective cracking of residual fuel, gas oil, and naphtha. In some plants, the residual fuel oil from the quench tower is fed to a low-pressure separator followed by vacuum distillation. Regardless of complexity, the major operations of cracking, quenching, and fractionation are present.

4. Pollution Sources

The major point sources of air pollution are shown in Figures 7 and 8. The cracking furnaces (point 1) are fired with fuel oil, natural gas, or refinery fuel gas. Stack gas emissions such as NO_x, SO_2, and particulates will be present. Cracking furnaces may also emit pollution during the maintenance shutdown period (point 2). Furnace tubes are cleaned with steam-air mixtures. Coke deposits contain sulfur and nitrogen. Removal of coke by burning will result in SO_2, NO_x, CO, and particulate emissions. Steam condensate will require stripping to remove sour constituents. Flue gases from cleaning operations may be routed to a furnace or otherwise incinerated to complete the combustion process. Mechanical cleaning of furnace tubes will greatly reduce the air pollution problems, but the refiner is then faced with a significant solids waste disposal problem.

Thermal cracking also serves as a desulfurization process, with the degree of desulfurization varying from 3% for mild visbreaking to 80% for severe thermal cracking. The sulfur is removed in the form of H_2S in the cracked gases (point 3), and these gases should be sent to an acid gas treating plant before being used for refinery fuel.

D. COKING

Coking is a thermal cracking process in which crude oil residue and other decanted oils and tar-pitch products are cracked at high temperature (900 - 1,080°F) and low pressure (atmospheric) into lighter products and petroleum coke. The objective is to produce gas oil and lighter petroleum stocks from the crude residue. These materials are further processed and blended with other stocks to produce premium products such as gasoline, jet fuels, and diesel fuels.

The crude oil residue feed to the coking unit contains most of the impurities of the crude oil. It contains most of the heavy metals (nickel, vanadium), essentially all the asphaltene, resin, and ash, 40% to 60% of the sulfur, and 80% to 90% of the nitrogen.

A rough estimate of the distribution of sulfur in coker products follows in Table 2.

Table 2. SULFUR CONTENT IN COKER PRODUCTS

Product	Percent of Feed Sulfur on Products
Fuel Gas	12
Coker Gasoline	3
Heavy Oils	25
Coke	60
	100

In the coking process, the residue is heated to a cracking temperature in which the longer hydrocarbon chains in the residue are severed into smaller more volatile components. These components evaporate at this high temperature and are collected and separated into the desired products by distillation. The asphaltene, resin, ash, metals, and residual carbon precipitate out of the liquid to form the highly cross-linked polymerized structure of the product coke. This process continues until all the volatile components are removed by vaporization and all the nonvolatile components have formed coke.

There are two principal coking processes: the fluid coking process and the delayed coking process. The most widely used is the delayed coking process and very few fluid coking units are now in service.

In the fluid coking process, the crude residue is fed to the reactor where it is mixed with recycled hot coke particles. The hydrocarbon portion of the liquid feed cracks and evaporates while the nonvolatile material is deposited on the suspended (fluidized) coke particles. The coke particles thus grow in size, sink to the bottom of the reactor and flow to the burner. In the burner, the particles are fluidized with air, partially burned and are recycled back into the reactor. A portion of the coke produced in the reactor is withdrawn as product.

A point source of pollutant emission is the burner. Emission control equipment could be similar to that used with fluid catalytic cracking units. Meeting new air pollution regulations may require the use of electrostatic precipitators and CO boilers.

In the delayed coking process (Figure 9), the charge stock is fed to the bottom section of the fractionator where material lighter than the desired end point of the heavy gas oil is flashed off. The remaining material combines with recycle and is pumped from the bottom of the fractionator to the coking heater where it is rapidly heated to above 900°F. The liquid-vapor mixture leaving the coking heater passes to a coke drum.

A unit usually has two drums with one being filled while the other is being decoked. Large units may have four or even six drums. The coke drums are most often sized so that each one operates on a 48-hour cycle, thus permitting decoking of a drum to be scheduled at the same time each day on a 24-hour cycle.

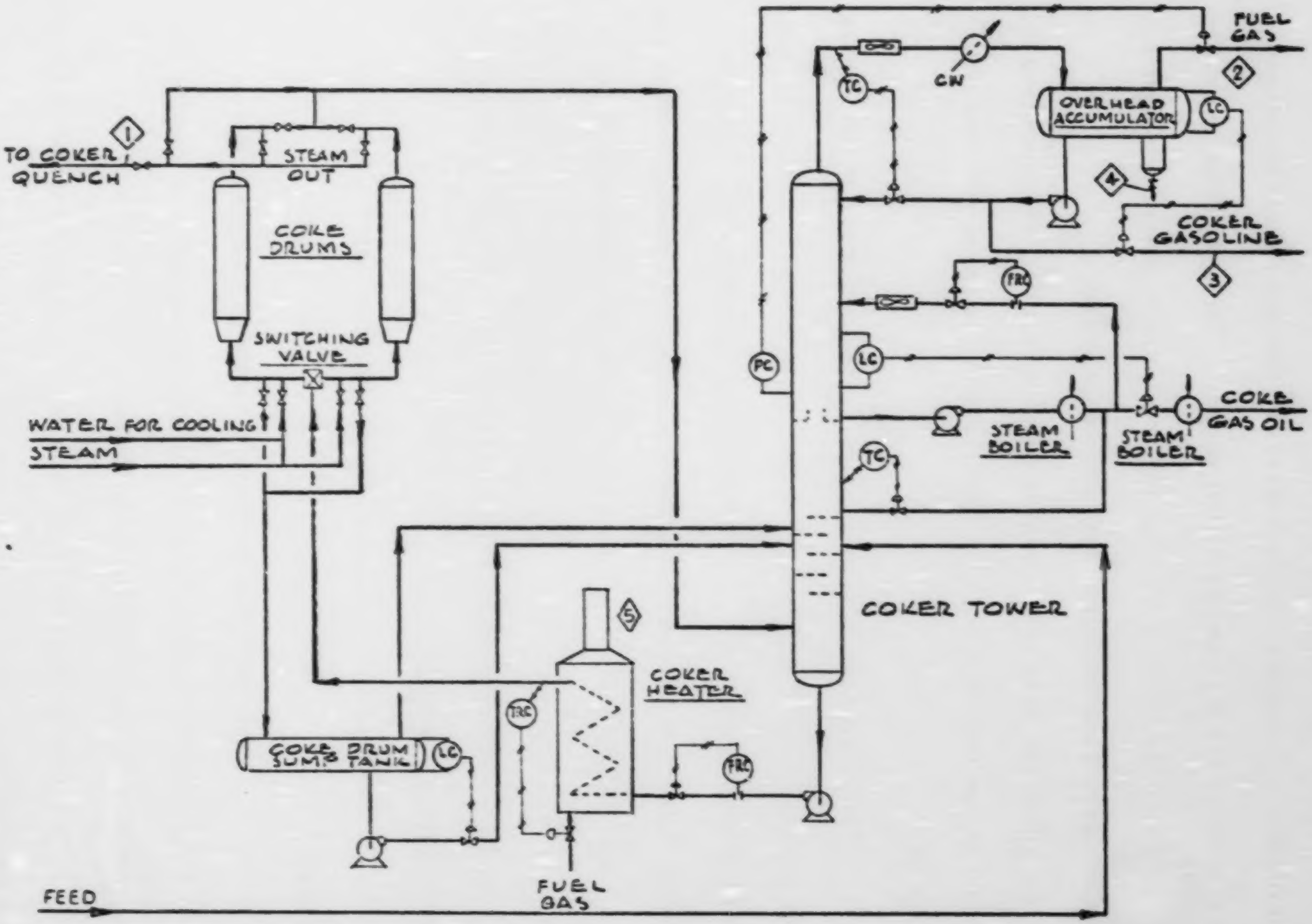

TO COKER QUENCH
1
STEAM OUT
COKE DRUMS
SWITCHING VALVE
WATER FOR COOLING
STEAM
COKE DRUM SUMP TANK
LC
TRC
5
COKER HEATER
FRC
FUEL GAS
FEED
COKER TOWER
PC
TC
LC
CW
OVERHEAD ACCUMULATOR
LC
FUEL GAS
2
4
COKER GASOLINE
3
FRC
STEAM BOILER
STEAM BOILER
COKE GAS OIL

Figure 9. Coking unit.

Under the time-temperature conditions in the drum, coke is formed and accumulates in the vessel and the more volatile components formed leave in the overhead vapors. The coke drum overhead vapors enter the lower section of the fractionating tower for separation into gas, gasoline, gas oils, and recycle stock.

After the first coke drum is filled with coke, the operation is shifted to the second drum and the first drum is ready for coke removal.

The initial step in coke removal is the cooling of the hot drum with steam. Live steam is blown into the drum where it absorbs heat, evaporates some hydrocarbon material and entrains some coke particles. After leaving the drum, the vapors are cooled to condense the steam and hydrocarbons. The cooled stream separates into three parts:

1. Water, with coke particles, that should be added to the coke removal system.

2. Hydrocarbon liquid that should be added to the slops system.

3. Noncondensables that normally go to a fired heater or a flare for disposal. This stream is primarily fuel gas and usually contains small amounts of sulfur compounds.

The second step is cutting the coke. A high-pressure water jet, 2,000 psi or more is used to cut the coke free from the drum. The coke particles are washed out with the water and are separated from the water on vibrating screens. Fines remaining in the water are removed in a thickener, and the water is recycled for cutting and transporting the coke.

Pollution Sources

Point sources of pollutant emission from this process include:

1. The steam from the steam-out operation, if not properly condensed and separated (point 1 in the figure).

2. Accumulator fuel gas is normally rich in H_2S. This stream has to be treated before entering the fuel gas system of the refinery (point 2).

3. Coker gasoline is normally treated for the removal of H_2S (point 3). (See Section M, Sweetening.)

4. Water drawn from the overhead accumulator contains H_2S and should be routed to a sour water stripper (point 4).

5. The fired heater is a source of pollution; see Chapter II (point 5).

6. Coking units are in general covered with coke dust. Unless the units are cleaned and washed thoroughly, these fine particles will blow with the wind and may create pollution.

7. Most delayed coking units use water for cutting the coke. The water is recycled in this operation and stored in open containers. Since this water contains some sulfur compounds, it may be the source of objectionable odors.

E. DEASPHALTING

Deasphalting is used to separate oil and asphalt. The feed stock is reduced crude from the crude distillation process. Reduced crude is the heavy fraction of the crude from which as much distillate has been removed as is practical with the existing crude unit. Deasphalting produces products comparable to those produced by high-vacuum distillation, but deasphalting is generally capable of more complete oil removal. A variation of the process is sometimes used to remove trace amounts of asphalt from lube-oil stocks.

Asphalt-oil separation is accomplished by selective extraction (liquid-liquid extraction) of the oil by a light hydrocarbon, usually propane. A heated mixture of reduced crude and liquid propane settles into two liquid phases, an upper phase containing oil and most of the propane and a lower phase containing the asphalt and some propane. The phases are separated, and propane is recovered for recycling by flashing and steam stripping.

Liquid-liquid extraction is a unit operation commonly used in refineries and chemical plants. In this operation, a mixture is separated into two components by means of a selective solvent. The addition of the solvent to the feed mixture must result in a two-phase mixture with an appreciable density difference between the two phases. The two phases will contain different ratios of the two feed components.

Although a single step of mixing and settling will produce some separation, multiple-step operations are frequently used to achieve more complete separation. Usually countercurrent extraction is employed, with solvent entering near one end of the column and feed at the other. The two liquid phases leave the column at the top and bottom. Mixing and settling within the column can be accomplished in several ways. Perforated plates or packing are often used, as well as mechanical agitators driven by a common shaft running through the column.

A flow diagram for a typical propane deasphalting process is shown in Figure 10. Reduced crude is metered to the process under flow control and passes through the feed heater where it is brought to operating temperature by indirect steam heat. The heated reduced crude is fed to the center of the extraction column where it is brought into contact with a rising stream of liquid propane. The propane, a recycle stream, is metered through a flow controller and through the propane heater into the bottom of the extraction column. Asphalt, containing some propane, leaves the bottom of the extractor under level control. The remaining propane and the extracted oil leave the top of the extractor. A steam coil in the upper section of the column is used to heat the rising propane-oil stream, reducing the solubility of asphalt in that stream. In this way, final traces of asphalt are removed from the oil, forming a separate phase that flows downward through the column.

The asphalt phase from the column passes through a furnace and then to a flash drum, where most of the propane is removed as a

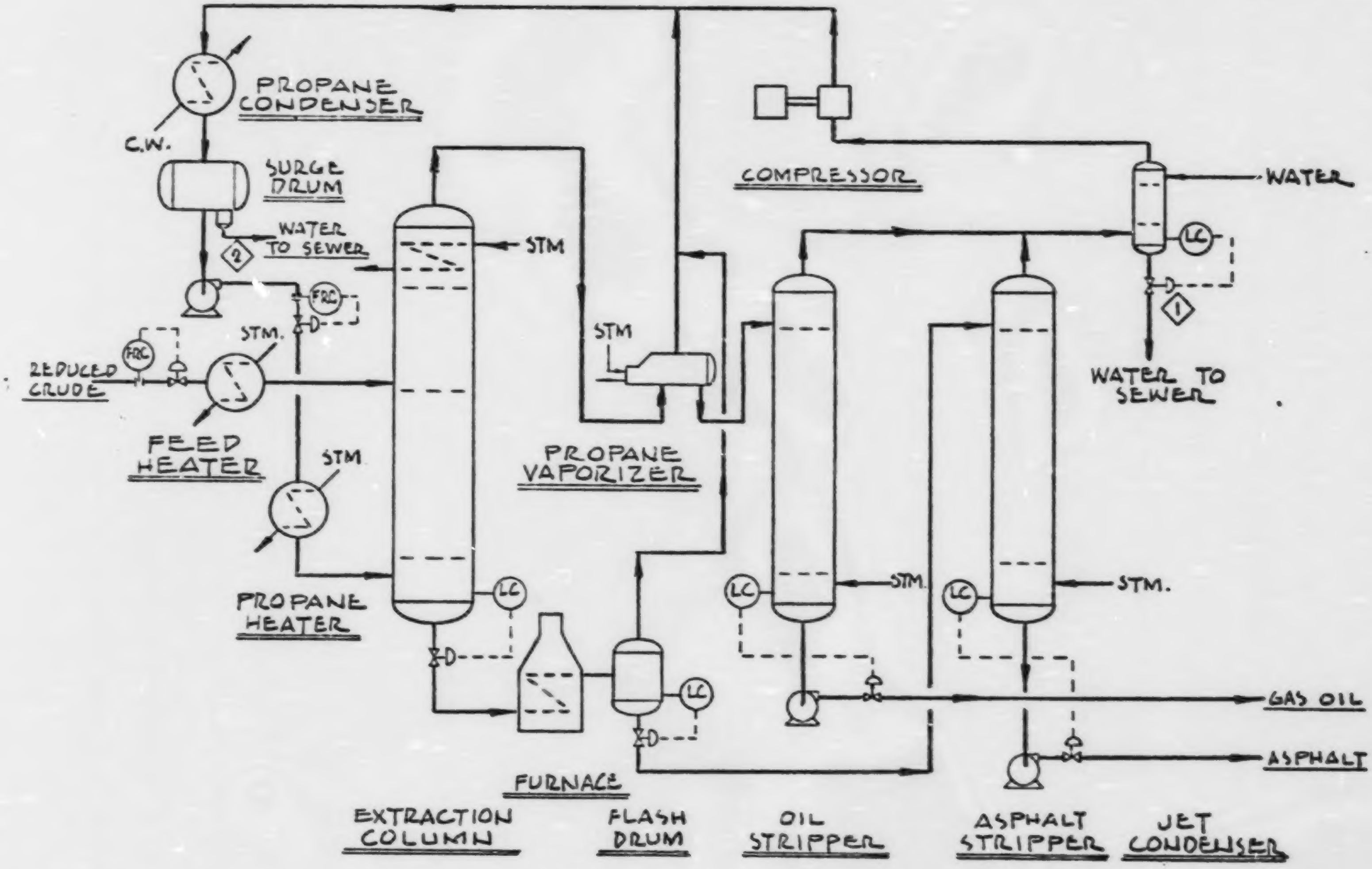

PROPANE CONDENSER
C.W.
SURGE DRUM
WATER TO SEWER
2
FRC
REDUCED CRUDE
FRC
STM.
FEED HEATER
STM
PROPANE HEATER
STM
LC
EXTRACTION COLUMN
FURNACE
FLASH DRUM
LC
STM
PROPANE VAPORIZER
COMPRESSOR
LC
STM.
OIL STRIPPER
LC
STM.
ASPHALT STRIPPER
WATER
LC
1
WATER TO SEWER
JET CONDENSER
GAS OIL
ASPHALT

Figure 10. Propane deasphalting.

vapor. Since the remaining asphalt still contains a small amount of propane, this stream is fed to the asphalt stripper. The remaining propane is steam stripped from the asphalt, and the asphalt product leaves the bottom of the stripper under level control. The stripping stream and propane leave the top of the stripper and pass through the jet condenser to condense the steam.

The oil-propane phase from the extractor is fed to a propane vaporizer, where the bulk of the propane is vaporized by indirect steam heating. The remaining propane is removed from the oil in the oil stripper by steam stripping. Product oil leaves the stripper under level control. The stripping steam and propane join the asphalt stripper overhead and are sent to the jet condenser.

Vaporized propane from the flash drum and the propane vaporizer are combined and sent directly to the propane condenser, where the propane is condensed to a liquid by cooling with water. The propane flows to a surge drum and is pumped back to the process as recycle. Steam and propane vapor entering the jet condenser are contacted with water to condense the steam. The water and condensed steam leave the bottom of the jet condenser and are sewered. The propane vapor leaves the top of the jet condenser at a pressure that is lower than that in the extraction section, so a compressor is used to send it to the propane condenser.

Pollution Sources

There are two potential sources of air pollution in this process that should be given special attention. One, point 1 on the flow diagram, is the water to sewer from the jet condenser. This stream will contain small amounts of propane and, depending on the character of the reduced crude feed, may also have an odor. The other potential source, point 2, is the water to sewer from the propane surge drum. This stream is small and may therefore be drained intermittently under manual control. The water will contain a small amount of dissolved propane, but more importantly, relatively large amounts of propane can be lost if the operator is careless about closing the valve after manually draining the water.

F. CATALYTIC CRACKING

There are two catalytic cracking processes in use today: the fluid catalytic cracking process which uses a powdered catalyst, and the Houdriflow or TCC process, no longer in general use, which uses a bead catalyst. Catalytic cracking is a high-temperature, low-pressure process which is used to convert gas oil feed stock into fuel gas, liquified petroleum gases (LPG), high octane gasoline, and distillate fuel.

Feed stocks to the catalytic cracking unit may be gas oils from the crude unit, thermally cracked gas oils, and/or deasphalted oils. The products from the reactor are given in Table 3. Catalytic cracking plants are normally operated to produce a maximum amount of gasoline, but the units are very flexible and operating conditions can be varied to produce other products.

Table 3. REACTOR PRODUCTS

Product	Wt. %
Water	1 to 2
Gas, C_2 and Lighter	3 to 7
Coke	3 to 8
Liquid Hydrocarbons	Remainder

1. The Fluid Catalytic Cracking Process

Figure 11 shows a schematic diagram of a typical fluid catalytic cracking unit. Gas oil feed is mixed with hot catalyst and introduced into the reactor. Steam is added at the base of the reactor to fluidize the catalyst bed and purge the spent catalyst. The volatile hydrocarbon products are withdrawn from the top of the reactor and sent to a fractionator where the product streams are separated.

The coke and catalyst are withdrawn from the base of the reactor and sent to a regenerator. A controlled amount of air is introduced into the regenerator with the catalyst to burn the coke and reheat the catalyst. The exhaust gas flows through a series of cyclone separators located inside the regenerator to remove the catalyst dust. An electrostatic precipitator or a third stage cyclone separator, located outside the regenerator, can be used to remove catalyst fines from the effluent gas.

The catalyst is continuously circulated from the reactor to the regenerator. The hot regenerated catalyst is returned to the reactor through a separate line into which the feed to the reactor is introduced.

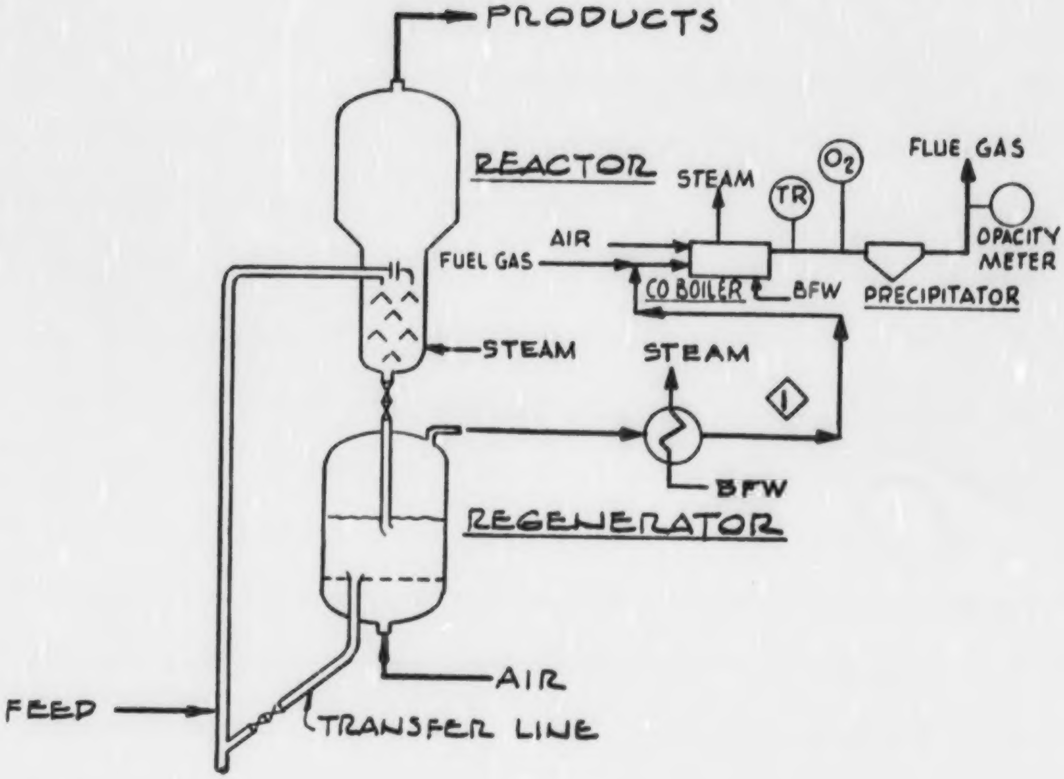

PRODUCTS
REACTOR
STEAM
TR
O2
FLUE GAS
AIR
FUEL GAS
OPACITY METER
CO BOILER
BFW
PRECIPITATOR
STEAM
STEAM
I
BFW
REGENERATOR
AIR
FEED
TRANSFER LINE

Figure 11. Fluid catalytic cracking unit.

Fresh catalyst is added to the system to keep up the activity of the reaction. Some catalyst is continuously lost to the atmosphere and constitutes a form of particulate pollution which should be controlled.

The flue gas from the regenerator contains five to ten percent carbon monoxide and can be burned to yield a considerable amount of heat energy. This gas can be burned in a boiler, with an auxiliary fuel, to generate steam. This procedure removes the toxic carbon monoxide gas from the flue gas and makes it suitable for discharge to the atmosphere. The boiler is usually monitored with suitable instrumentation to assure that complete combustion of the carbon monoxide occurs.

Pollution Sources

The catalytic cracking process converts about half of the sulfur in the feed stock to hydrogen sulfide. Part of this material appears in the condensate from the fractionator and from the gas plant. The wastewater is saturated with the gas and must be treated in a sour water treating process as discussed in Section C, Sour Water Stripping.

Some of the sulfur stays with the coke and is ultimately burned to SO_2 in the regenerator. The effluent gas from the regenerator (point 1 on the figure) may contain the following contaminants:

Aldehydes
Ammonia
Carbon dioxide
Carbon monoxide
Catalyst fines
Hydrocarbons
Oxides of nitrogen
Sulfur dioxide
Sulfur trioxide

The amount of each contaminant will vary with the type of plant and the effectiveness of pollution controls in the plant. Aldehydes, ammonia, carbon monoxide and hydrocarbons are controlled by combustion in a CO boiler. Catalyst fines are controlled by an electrostatic precipitator. The remaining pollutants are not controlled at present.

2. Catalytic Cracking with Bead Type Catalysts

Figure 12 is a schematic diagram of a typical moving bed catalytic cracking process. This type of plant can operate with a wide variety of feed stocks to maximize production of either gasoline or burning fuels. The process employs a moving bed of hot catalyst beads which flow downward from a surge hopper into a reactor where the beads contact fresh gas oil feed. The gas oil is cracked yielding a mixture of hydrocarbons known as synthetic crude. The descending bed of catalyst is purged with steam at the base of the reactor. The mixture of steam and cracked gases flows from the reactor to a system of fractionating columns which separate it into fuel gas, LPG, gasoline, gas oil, and water. The catalyst drops from the reactor into the regenerator where air is used to burn off the coke which has deposited on the beads.

Pollution Sources

The flue gas from the regenerator (point 1 in the figure) is similar to that from a fluid catalytic cracking unit. A precipitator or cyclone separator can be used to remove catalyst fines, although the problem is not as severe as with fluid units. The flue gas can be burned in a waste heat boiler to eliminate the carbon monoxide.

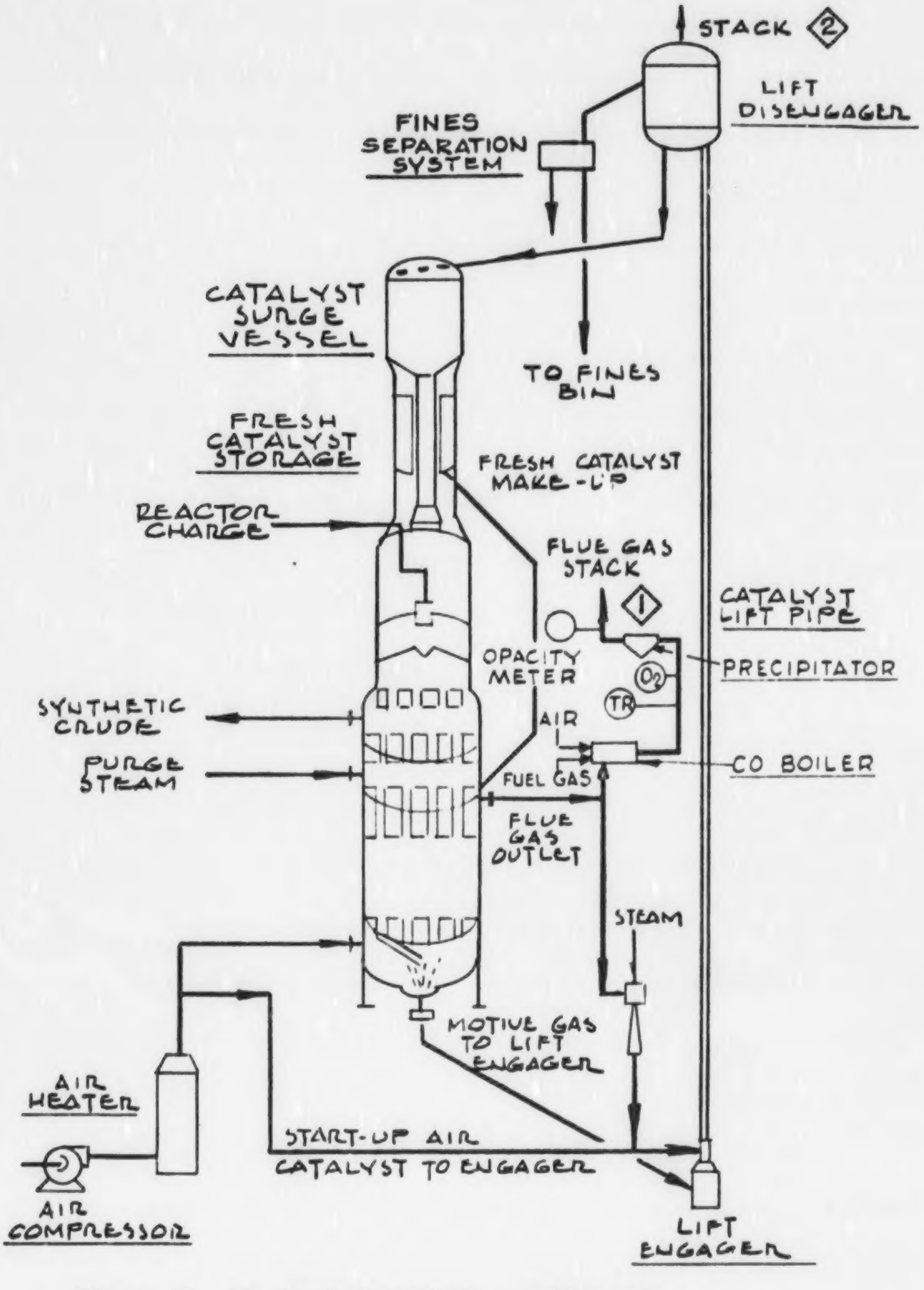

STACK
②
LIFT DISENGAGER
FINES SEPARATION SYSTEM
CATALYST SURGE VESSEL
TO FINES BIN
FRESH CATALYST STORAGE
FRESH CATALYST MAKE-UP
REACTOR CHARGE
FLUE GAS STACK
①
CATALYST LIFT PIPE
OPACITY METER
PRECIPITATOR
O2
TR
SYNTHETIC CRUDE
AIR
PURGE STEAM
FUEL GAS
CO BOILER
FLUE GAS OUTLET
STEAM
MOTIVE GAS TO LIFT ENGAGER
AIR HEATER
START-UP AIR
CATALYST TO ENGAGER
AIR COMPRESSOR
LIFT ENGAGER

Figure 12. Moving bed catalytic cracking unit.

Another possible source of particulate pollution is the catalyst transfer system. The catalyst is lifted from the regenerator outlet to the catalyst feed hopper with a pneumatic lift. A disengaging drum at the top of the lift recovers the catalyst, but some catalyst fines may be discharged to the atmosphere from this source (point 2) if it is not controlled.

3. Control Strategies

a. CO Boiler:

Excess CO in Flue Gas - Increase air to CO boiler.
Excess SO_2 in Flue Gas - Reduce sulfur in feed stock.

b. Electrostatic Precipitator

Excess Fines in Flue Gas from Fluid Unit - Inspect and clean fines removal equipment.
- Increase fines withdrawal from the plant at the precipitator.

G. ALKYLATION

Alkylation is a process in which an olefin hydrocarbon reacts with an aromatic or a paraffinic hydrocarbon. An acid catalyst is used to reduce the temperature and pressure required for the reaction to proceed. Alkylation units are used to produce high octane gasoline components and synthetic chemicals such as cumene and ethyl benzene.

The two principal materials currently being used as alkylation catalysts are sulfuric acid and hydrofluoric (HF) acid. There are about 140 alkylation units in operation in the United States, with the number of units of each type being about equal. Both processes operate at moderate temperatures and pressures as shown in Table 4.

Table 4. ALKYLATION PROCESSES OPERATING TEMPERATURES AND PRESSURES

Process Catalyst	Temperature °F	Pressure psig
Sulfuric Acid	30 - 50	5
Hydrofluoric Acid	75 - 105	125

Both acids are highly corrosive, and the containment systems are prone to develop leaks.

1. The Sulfuric-Acid Process

Figure 13 is a schematic diagram of a typical sulfuric acid alkylation process. The feed stream could be a mixture of an olefin such as butene and a paraffin hydrocarbon such as isobutane. The two streams are mixed and introduced into a horizontal staged reactor. A circulating stream of sulfuric acid and isobutane flows through the reactor. The reaction of the hydrocarbons is exothermic, and vapor is withdrawn and condensed to cool the reactor. The hydrocarbon liquid from the reactor is washed with caustic and water and then fractionated to separate the alkylate product from the isobutane which is returned to the reactor. The process shown uses autorefrigeration. It is also possible to cool the reaction by indirect cooling.

The spent acid (point 1 in the figure), which may be shipped off-site for regeneration, is saturated with volatile hydrocarbons which

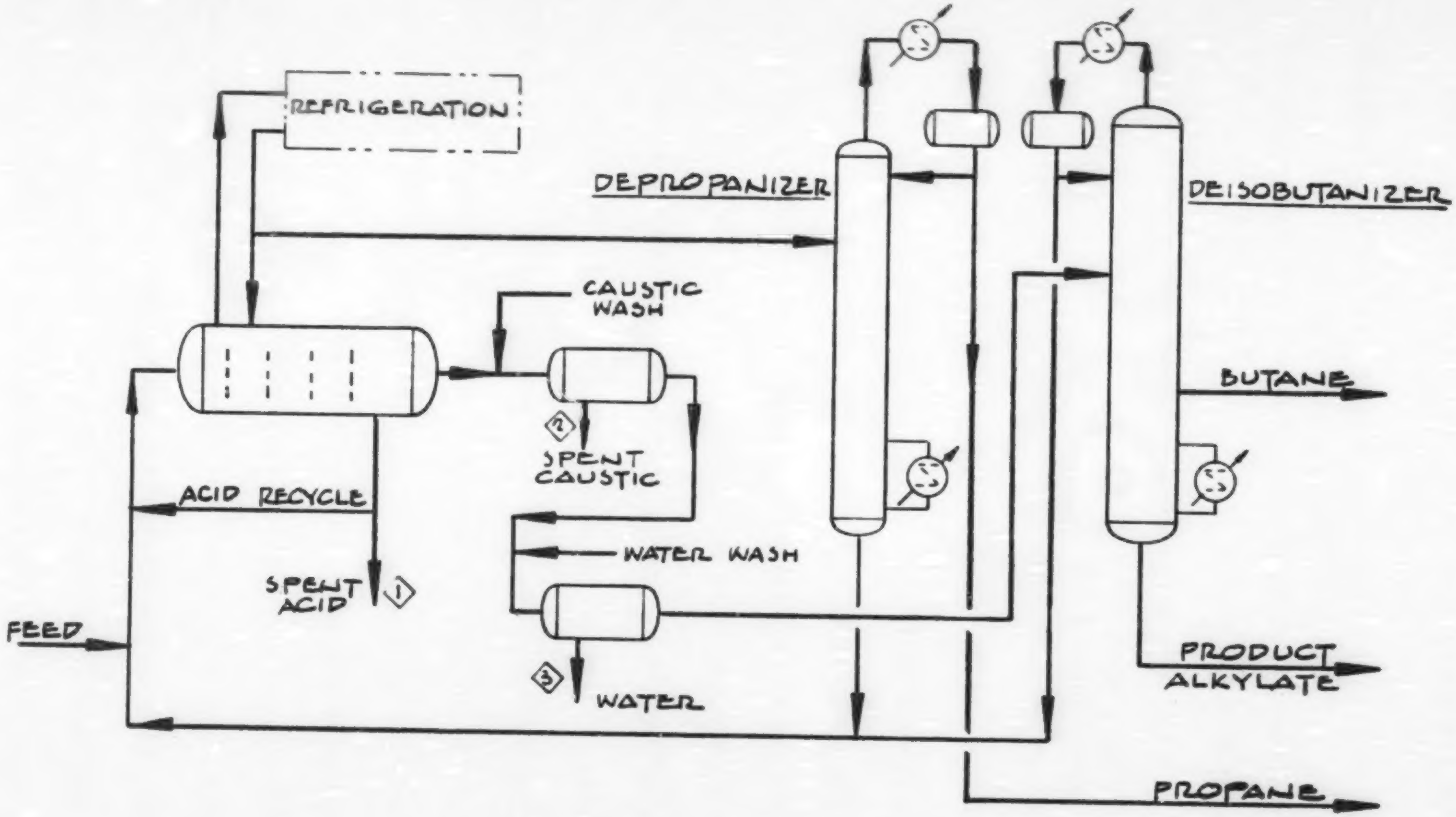

REFRIGERATION
DEPROPANIZER
DEISOBUTANIZER
CAUSTIC WASH
SPENT CAUSTIC
2
ACID RECYCLE
WATER WASH
SPENT ACID
1
FEED
3
WATER
BUTANE
PRODUCT ALKYLATE
PROPANE

Figure 13. Sulfuric acid alkylation process.

should be contained. The spent caustic (point 2) and water (point 3) streams may also entrain some hydrocarbon which will vaporize if the stream is discharged to the atmosphere. These sources should be confined to prevent atmospheric pollution.

2. The Hydrofluoric Acid Process

Figure 14 is a schematic diagram of a typical HF acid alkylation plant. The hydrocarbon feed to the plant is mixed with hydrofluoric acid in a reactor. The mixture is settled and the hydrocarbon product fractionated to produce recycle isobutane and product alkylate. A small acid stripping column regenerates the catalyst and gives a by-product tar which may be burned (point 1 on the figure). A stripping column is provided to separate an acid rich fraction, which is recycled, from the LPG product which is washed with caustic and water. The caustic waste (point 2) and the sour water (point 3) should not be vented to the atmosphere.

Hydrofluoric acid is a volatile liquid which is toxic and corrosive. HF lines may be jacketed to contain any possible leakage, and a water spray or alkali dump system is usually provided in the event that a mechanical failure should release any of the acid.

3. Pollution Sources

The principal source of pollution from either type of alkylation plant during normal operation would result from atmospheric disposal of spent caustic and water streams (points 2 and 3 on the figures) and these streams should be confined with vapors vented to flare.

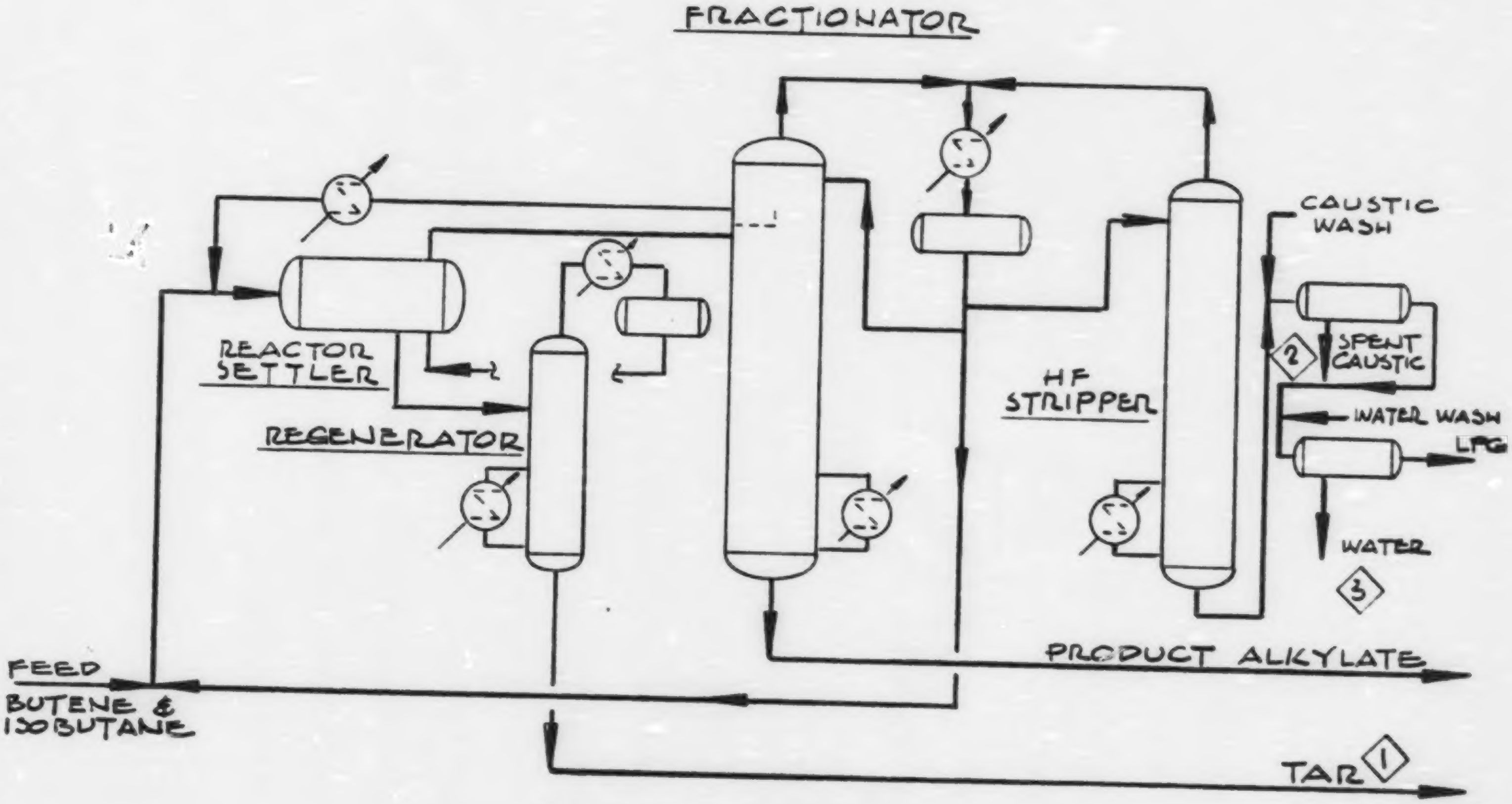

FRACTIONATOR
REACTOR SETTLER
REGENERATOR
HF STRIPPER
CAUSTIC WASH
2
SPENT CAUSTIC
WATER WASH
LPG
WATER
3
FEED
BUTENE & ISOBUTANE
PRODUCT ALKYLATE
TAR
1

Figure 14. HF alkylation process.

Hydrocarbon and, more particularly, HF leaks are a potential source of serious air pollution. Tar from HF alkylation (point 1, Figure 14) is often disposed of by incineration. This may be a source of pollution if the burning is not properly controlled.

H. ISOMERIZATION

Isomerization is used to upgrade normal paraffins (straight-chain hydrocarbons) to isoparaffins (branched chain). The process is usually applied to butane or to mixtures of pentane and hexane. Where butane is the feed stock, the isobutane product is normally used as feed to an alkylation unit. Pentane-hexane feeds, from crude distillation or catalytic reforming, are processed to improve their octane ratings, and the product is blended to gasoline.

Two methods have been used to bring about the isomerization reaction in petroleum refining. The old method used aluminum chloride in either vapor or liquid-phase reactions, but this practice is now obsolete. The new method employs noble metal catalysts on a solid catalyst support, and the feed is mixed with hydrogen to suppress unwanted reactions.

Figure 15 is a schematic diagram for a butane isomerization process. Since the butane feed usually contains a mixture of normal and isobutane, the mixture is first separated into its normal and iso components by distillation in the deisobutanizer. The overhead product, isobutane, is sent to storage or directly to an alkylation unit. The

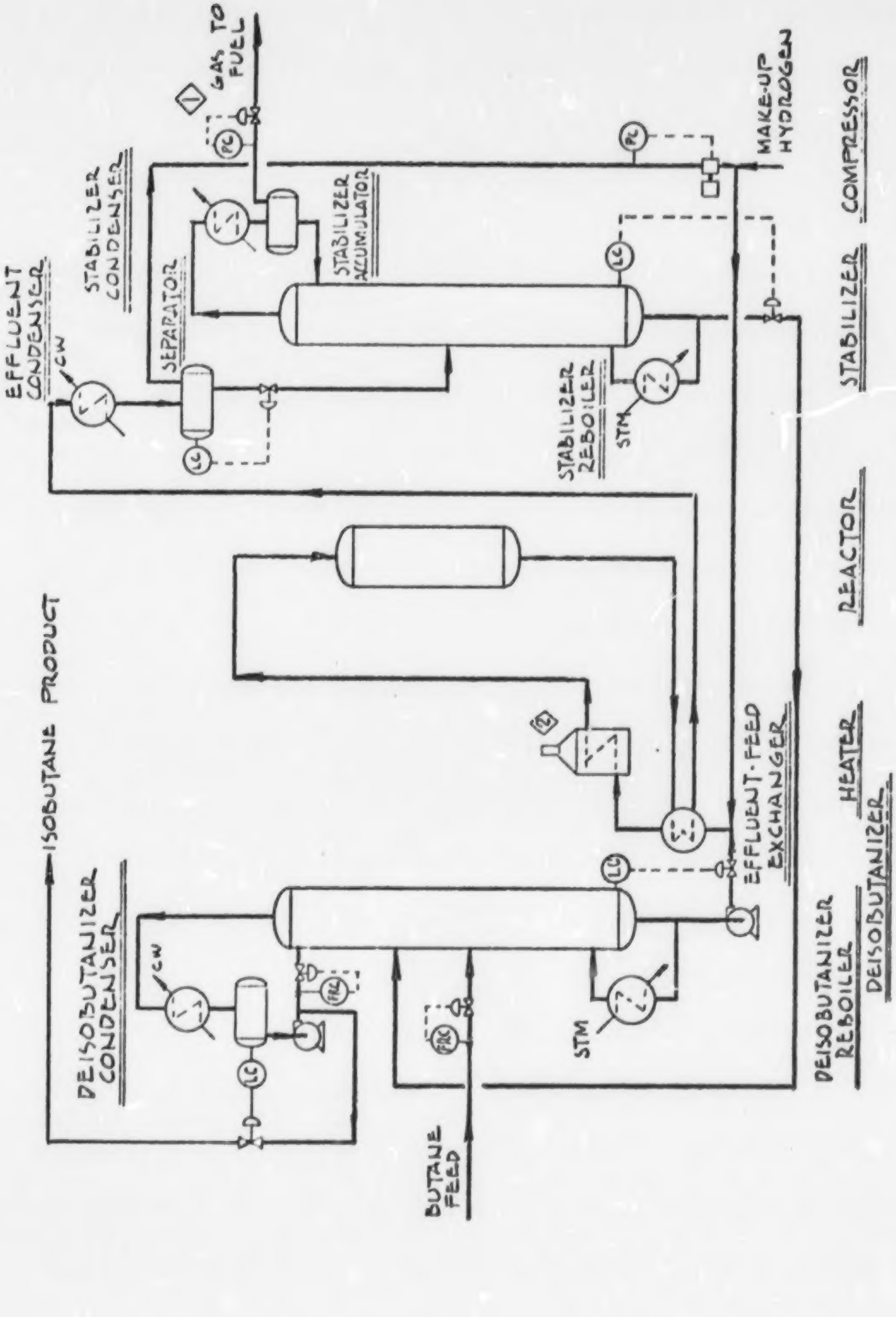

ISOBUTANE PRODUCT
DEISOBUTANIZER CONDENSER
CW
LC
FRC
STM
BUTANE FEED
EFFLUENT-FEED EXCHANGER
LC
EFFLUENT CONDENSER
CW
STABILIZER CONDENSER
SEPARATOR
STABILIZER ACCUMULATOR
GAS TO FUEL
PC
PC
MAKE-UP HYDROGEN
LC
STABILIZER REBOILER
STM
DEISOBUTANIZER REBOILER
DEISOBUTANIZER
HEATER
REACTOR
STABILIZER
COMPRESSOR

Figure 15. Butane isomerization.

bottom product, normal butane, is mixed with hydrogen and heated by indirect heat exchange with reactor effluent.

The feed stream is further heated in the fired heater and then passed over the catalyst in the reactor. Reactor effluent is cooled, first by exchange with the feed and then in a water-cooled effluent condenser. The condenser is followed by a separator in which the liquid and gas phases are separated.

The gas phase from the separator, primarily hydrogen, is recycled to the reactor by means of the compressor. The liquid phase contains dissolved hydrogen and other gases, which are removed in the stabilizer. The stabilizer is a distillation column in which all liquid reflux is returned to the column. Gas from the stabilizer accumulator is sent to the fuel gas system. Stabilizer bottoms is a mixture of iso and normal butane and is, therefore, fed to the deisobutanizer for separation into isobutane product and normal butane. Normal butane is recycled until it is converted to isobutane.

The following procedure is used for regeneration in place. The unit is shut down, and the reactor is depressurized to the refinery flare system. Inert gas, supplied by an inert gas generator, is used to free the reactor of combustible gas. The catalyst is brought to temperature by recycling inert gas through the heater and reactor, and carbon is burned off the catalyst by adding a controlled amount of air to the circulating gas stream. Since the gas stream contains products of incomplete combustion, it is good practice to incinerate the off gas that is bled from the system to balance the air added. This off gas can be incinerated in the fired heater.

Pollution Sources

Since the feed to this process must be nearly sulfur free in order to protect the catalyst, there is no problem with hydrogen sulfide contaminated gas streams. There is, however, a possible potential source of air pollution in the gas-to-fuel stream (point 1 in the figure). In some versions of the isomerization process, particularly with pentane-hexane feed, an organic chloride is added to the feed to increase catalyst activity. This chloride eventually shows up in the vapor streams as hydrogen chloride. Most of the hydrogen chloride is recycled to the process, but some of it is eliminated with the gas-to-fuel stream. In such cases, this stream should be treated to remove the hydrogen chloride before the gas is burned as fuel. Sometimes a caustic scrubber is used for this purpose.

The combustion gases from the reactor feed heater (point 2) are a source of air pollution (see Chapter II).

Another potential source of air pollution is the off gases from catalyst regeneration, not shown in Figure 15. The catalyst used in isomerization is very stable and can be expected to last for two years or more before regeneration is required. In fact, some refineries do not regenerate the catalyst, preferring to replace it and return the spent catalyst to the manufacturer.

I. HYDROTREATING

Hydrotreating or hydrodesulfurization processes are used to remove sulfur from liquid petroleum fractions. Some nitrogen removal and saturation of olefin bonds may also occur. Sulfur removal is accomplished by reacting the sulfur containing compounds with hydrogen in the presence of a catalyst to form hydrogen sulfide. The hydrogen sulfide is separated by simple vapor-liquid separation.

The processes have been applied to a full range of feeds, from gasoline to fuel oil. Reaction temperature is normally kept within the range of 600 to 750°F, while pressures are in the range of 300 to 500 psig for easily treated fractions and from 700 to 1,000 psig for fractions requiring more severe treatment.

Figure 16 is a diagram of a typical hydrotreating process. The hydrocarbon feed is heated in an exchanger and mixed with a hydrogen-rich gas stream. The mixed feed is heated in a fired heater and passed through a catalyst bed, where the hydrogen reacts with sulfur and nitrogen compounds. Reactor effluent is cooled and a small quantity of water is added to absorb ammonia compounds. The liquids are separated from the vapors, and the water phase is withdrawn. The hydrocarbon liquids are fractionated into separate product streams.

Pollution Sources

Possible point sources of pollutant emission are:

The water phase (points 1, 2, and 3 in the figure) contains

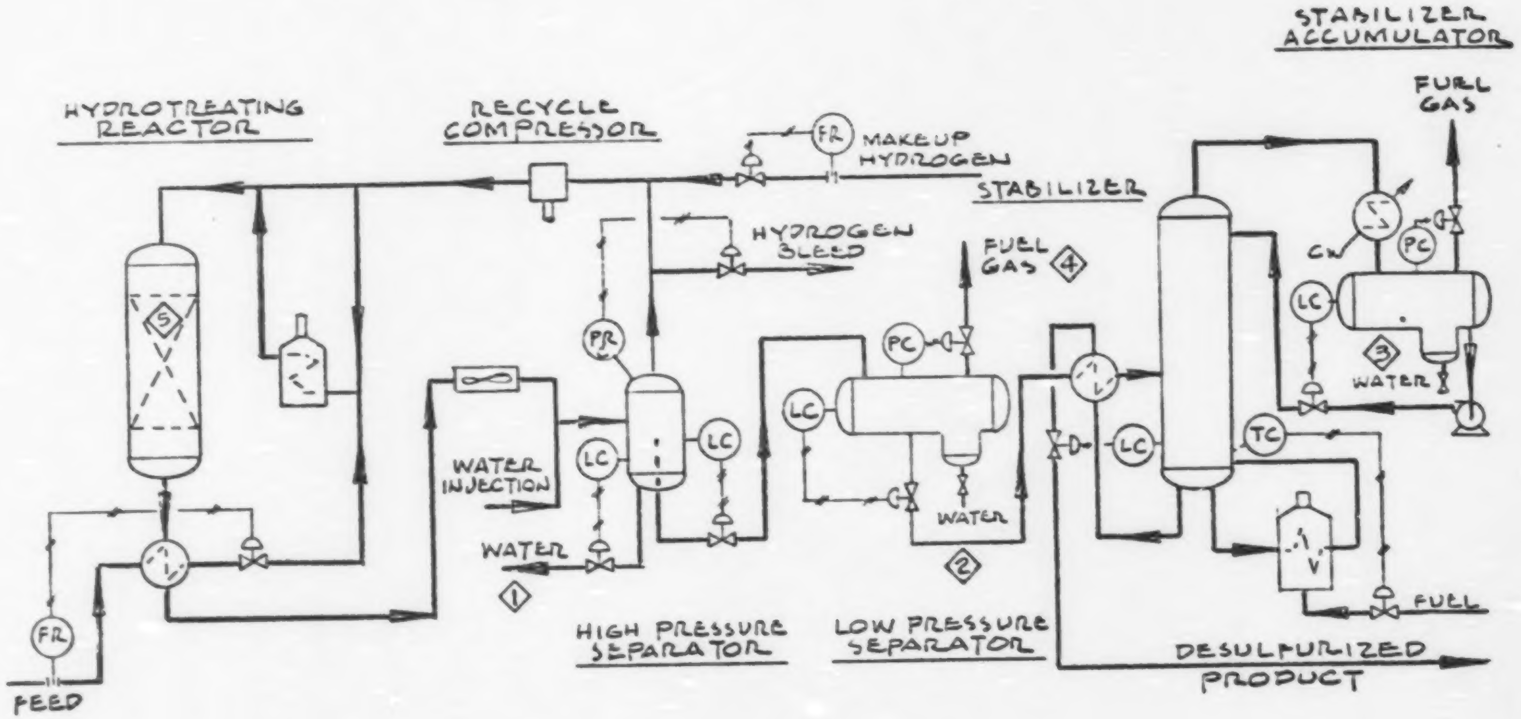

STABILIZER ACCUMULATOR
HYDROTREATING REACTOR
RECYCLE COMPRESSOR
FR
MAKEUP HYDROGEN
STABILIZER
FUEL GAS
HYDROGEN BLEED
FUEL GAS
4
PC
CW
LC
5
PR
3
WATER
TC
LC
LC
LC
LC
WATER INJECTION
WATER
WATER
1
2
FUEL
FR
HIGH PRESSURE SEPARATOR
LOW PRESSURE SEPARATOR
DESULFURIZED PRODUCT
FEED

Figure 16. Hydrotreating.

ammonia and hydrogen sulfide and should be sent to a sour water treatment plant.

The gas phase (point 4) contains hydrogen, methane, and hydrogen sulfide and should be treated to remove H_2S before being used for fuel gas.

The catalyst loses its activity due to the accumulation of carbonaceous deposits and to the deposition of trace metals. As the unit continues to operate the pressure drop across the bed builds up and eventually the process must be shut down. The catalyst may be regenerated by burning off the carbonaceous material (point 5), or it may be replaced by new catalyst. With a mild treatment, regeneration may be required at yearly intervals, but where treatment conditions are severe and with the older type catalysts, regeneration will be required at more frequent intervals. (See Section BB, Catalyst Regeneration.)

J. REFORMING

Catalytic reforming is used by refineries to economically upgrade low octane naphthas to produce premium quality motor fuels, high yields of aromatic hydrocarbons, high quality aviation gasoline components, and liquified petroleum gases. The reactions involved in reforming normally result in the production of hydrogen which is used either in other refinery processes or in the plant fuel gas system.

A typical reforming process design is shown in Figure 17. Prior to reforming, the naphtha is hydrotreated for the removal of

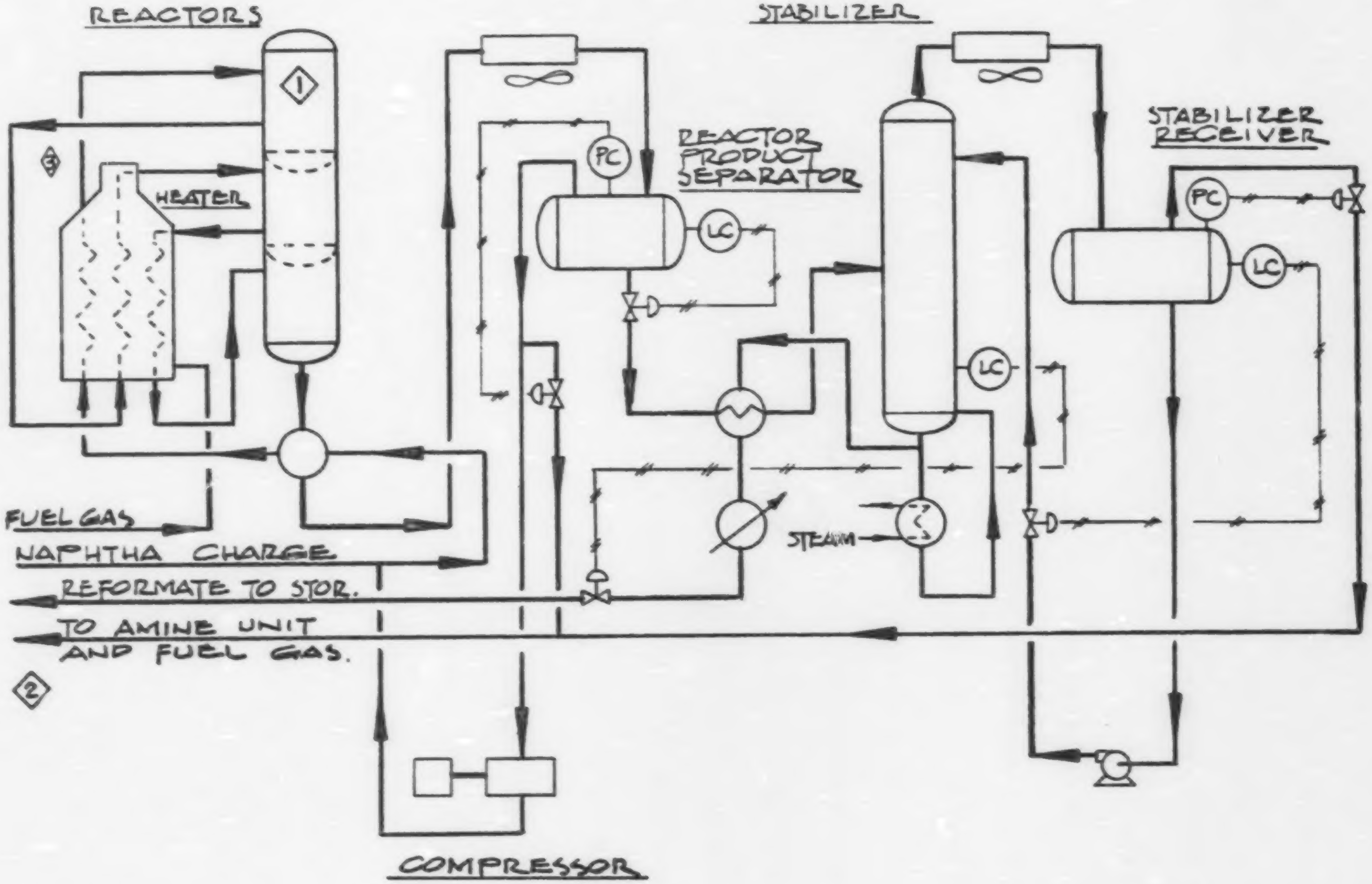

REACTORS
①
③
HEATER
FUEL GAS
NAPHTHA CHARGE
REFORMATE TO STOR.
TO AMINE UNIT
AND FUEL GAS.
②
PC
LC
REACTOR
PRODUCT
SEPARATOR
STABILIZER
LC
STEAM
STABILIZER
RECEIVER
PC
LC
COMPRESSOR

Figure 17. Reforming.

essentially all the sulfur in the feed. (See Section I, Hydrotreating Processes.) Sulfur free naphtha charge and hydrogen rich recycle gas are heated in a furnace to reactor inlet temperature and then passed through catalyst beds in a series of reactors. As the major reactions are endothermic, the gas temperature drops across each reactor and furnaces are required to reheat the gas between the reactors. The effluent gas is condensed and separated into a liquid stream and hydrogen rich gas. The liquid is processed through the stabilizer and withdrawn as finished reformate. A portion of the gas is recycled and the remainder used as either a source of hydrogen for other processes or fuel.

A number of reforming processes are currently in use, but the basic process is that shown in the figure. The major differences between the processes are in the composition of the catalyst used in the reactors and in the methods for regenerating the catalyst. Until recently, catalyst beds were fixed and were regenerated in place. However, continuously regenerated beds have now been introduced. Catalyst regeneration is required because coke is deposited on the catalyst surface during normal operation. This results in reduced catalyst activity. During regeneration, the coke is burned off the catalyst under carefully controlled conditions.

Pollution Sources

The gases evolved during regeneration may contain air pollutants and should be incinerated (point 1). (See Section BB, Catalyst Regeneration.)

The fuel gas stream contains hydrogen sulfide and is a potential source of air pollution (point 2). The fuel gas stream is sent to an amine unit where hydrogen sulfide is removed.

Combustion gases from the heater (point 3) are another source of air pollutant emissions.

K. HYDROCRACKING

Hydrocracking is used to convert heavy feed stocks into lighter, more valuable products. In this cracking process, the feed stock is converted into shorter chain hydrocarbon molecules in the presence of hydrogen and a catalyst. The feed stock to the hydrocracking unit is normally gas oil or middle distillate, and the usual products are fuel gas, gasoline, and jet fuel. The process is flexible in that the production of either gasoline or jet fuel can be maximized as needed.

Hydrocracking employs high pressure (1, 500 to 3, 000 psi), high temperatures (500 to 750°F), and a special catalyst. The reaction section is usually divided into two stages. The first stage is used to remove all the nitrogen and sulfur (see Hydrotreating), while the second stage is used for cracking. The first stage is needed in most cases because sulfur and nitrogen are catalyst poisons for the cracking catalyst used in the second stage. However, a single-stage reaction section is sometimes used where the feed stock is low in sulfur and nitrogen. Single-stage catalysts are more sulfur-resistant than those used in the second stage of a two-stage unit.

Figures 18 and 19 are flow diagrams of a reaction section and a distillation section of a typical hydrocracking unit. The feed is pretreated and cracked in the reaction section, and products are recovered in the distillation section.

Gas oil and/or distillate feed containing some sulfur and nitrogen impurities is pumped from the feed drum and heated by exchange with the first reactor product. Hydrogen is added to the feed and additional heat is supplied by a fired heater. The feed enters the reactor at about 3,000 psi and 700°F. The reaction is exothermic (heat producing) and the temperature is maintained by cooling the reactor catalyst beds by adding cold hydrogen. The reaction products are cooled, water is injected into the product stream and the reaction products and water stream enter the high pressure separator.

At this point all of the sulfur in the feed has been converted to H_2S and all the nitrogen in the feed to NH_3. The approximate distribution of sulfur (H_2S) and nitrogen among the streams leaving the high-pressure separator is shown in table 5.

Table 5. SULFUR AND NITROGEN DISTRIBUTION IN THE HIGH PRESSURE SEPARATOR

Product	Wt. % Feed	
	Sulfur	Nitrogen
Hydrogen rich gas	50	Nil
Hydrocarbon liquid	40	5
Water	10	95
Total	100	100

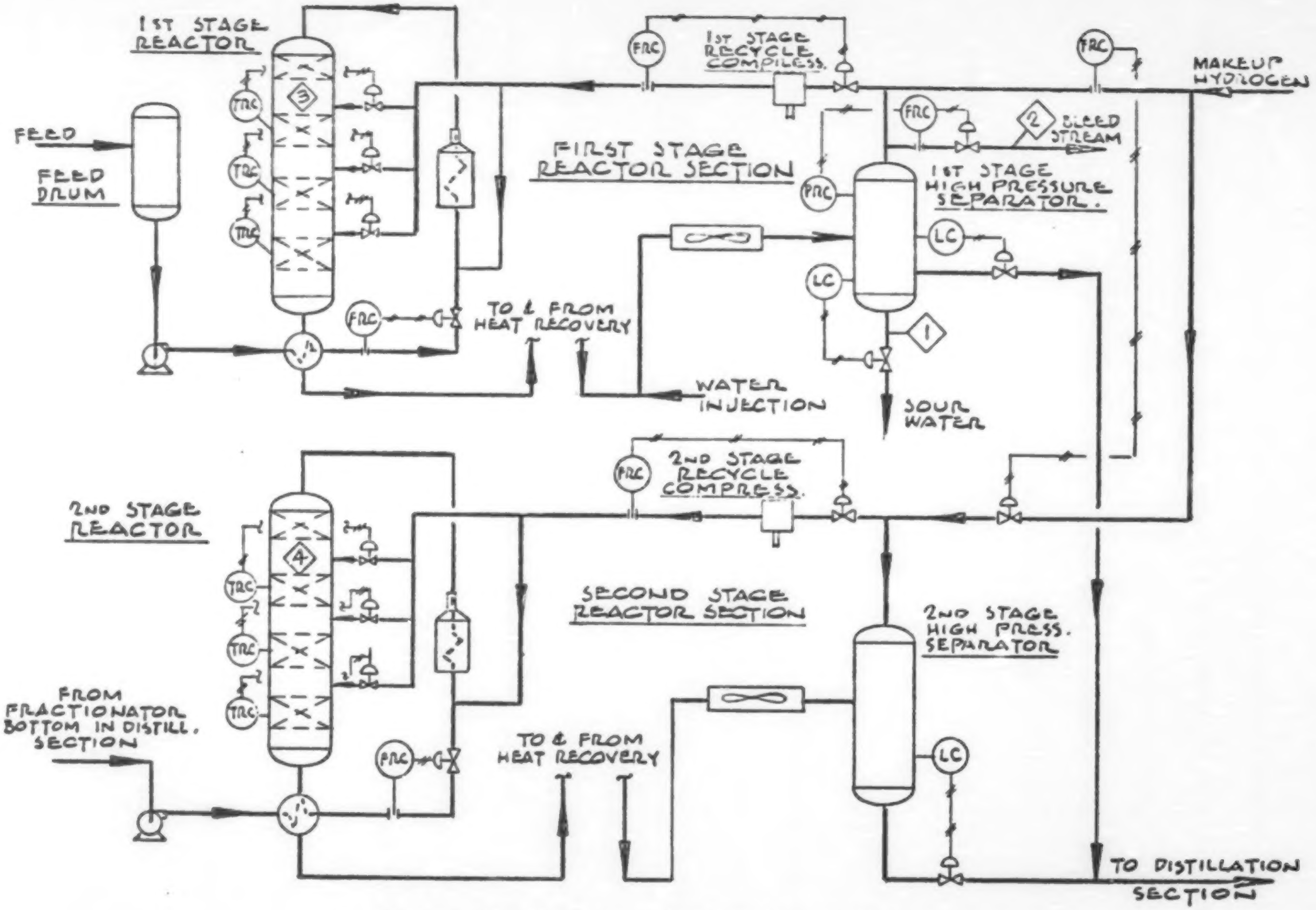

1ST STAGE REACTOR
FEED
FEED DRUM
3
TRC
TRC
TRC
FRC
1ST STAGE RECYCLE COMPRESS.
FRC
MAKEUP HYDROGEN
FRC
2
BLEED STREAM
FIRST STAGE REACTOR SECTION
PRC
1ST STAGE HIGH PRESSURE SEPARATOR.
LC
LC
1
FRC
TO & FROM HEAT RECOVERY
WATER INJECTION
SOUR WATER
2ND STAGE REACTOR
4
TRC
TRC
TRC
PRC
2ND STAGE RECYCLE COMPRESS.
SECOND STAGE REACTOR SECTION
2ND STAGE HIGH PRESS. SEPARATOR
LC
FROM FRACTIONATOR BOTTOM IN DISTILL. SECTION
PRC
TO & FROM HEAT RECOVERY
TO DISTILLATION SECTION

Figure 18. Hydrocracking reaction section.

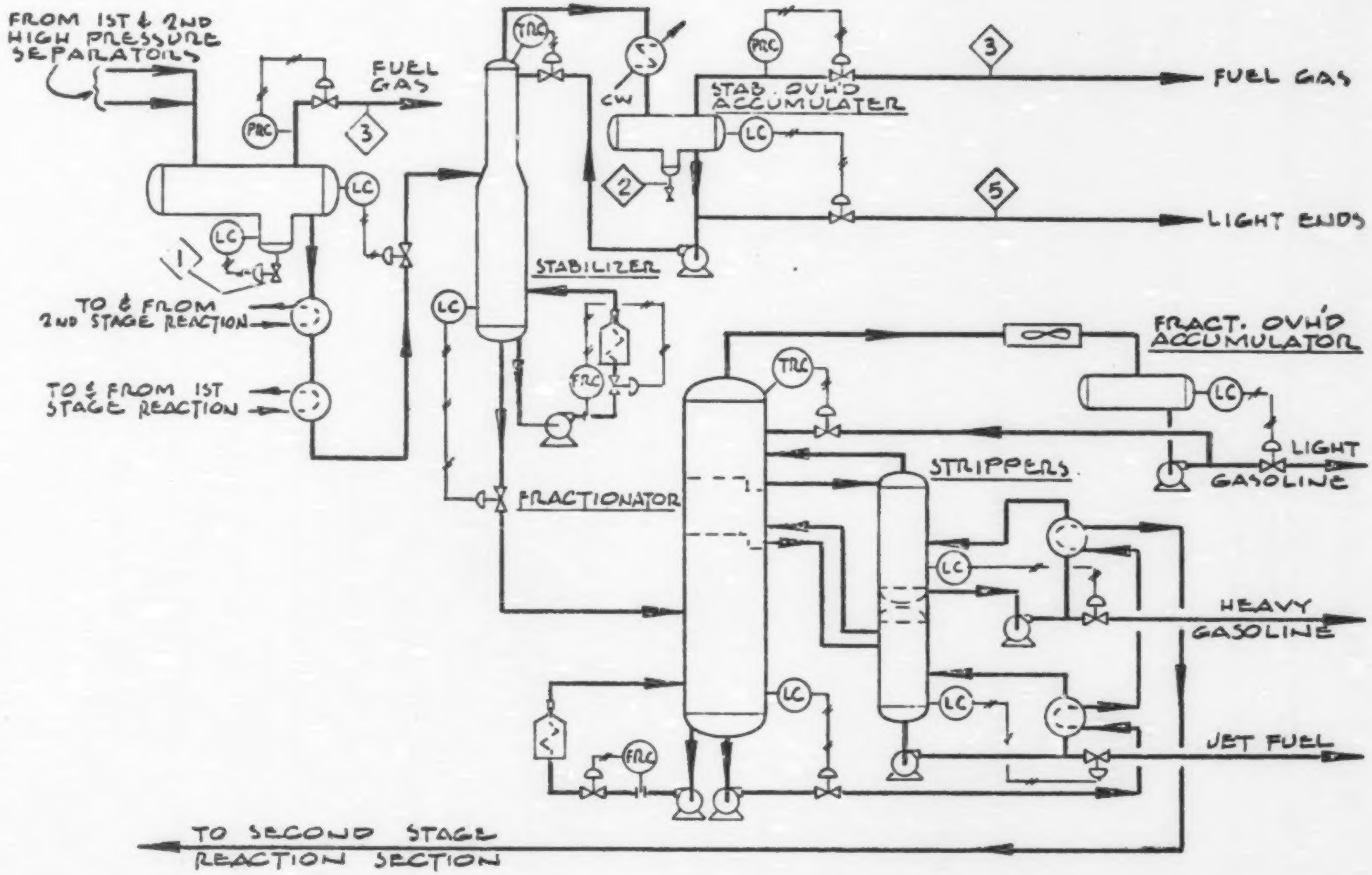

FROM 1ST & 2ND HIGH PRESSURE SEPARATORS
FUEL GAS
PRC
3
LC
LC
1
TO & FROM 2ND STAGE REACTION
TO & FROM 1ST STAGE REACTION
TRC
LC
STABILIZER
FRC
CW
PRC
STAB. OVH'D ACCUMULATER
LC
2
3
FUEL GAS
5
LIGHT ENDS
FRACTIONATOR
TRC
FRACT. OVH'D ACCUMULATOR
LC
LIGHT GASOLINE
STRIPPERS
LC
HEAVY GASOLINE
LC
JET FUEL
LC
FRC
TO SECOND STAGE REACTION SECTION

Figure 19. Hydrocracking distillation section.

The hydrocarbon liquid from the first-stage high-pressure separator is combined with the liquid from the second-stage high-pressure separator and is fed to the stabilizer in the distillation section to separate products from unreacted feed. The hydrogen rich gas from the first-stage high pressure separator is recycled back to the reactor with the addition of sufficient makeup hydrogen to replace that consumed by the reaction. Hydrogen purity is maintained by sending a bleed stream to a H_2S absorber.

Fractionator bottom liquid from the distillation section is unreacted feed. This stream is fed to the second reaction stage. Process flows in the second reaction stage are the same as in the first reaction stage except that no sulfur or nitrogen is present in the feed. Cracking occurs at 1, 500 psi and 600° F.

The distillation section is similar to those used in other cracking processes such as fluid catalytic cracking and thermal cracking. The total flow from both high pressure separators is fed to the low pressure separator in the distillation section. The pressure is reduced and fuel gas is flashed out of the hydrocarbon fluid.

The low-pressure separator liquid is fed to the stabilizer. In the stabilizer, all the light ends and the H_2S are stripped out and are taken overhead. Both the gas and the light ends (overhead) liquid have to be treated for the removal of H_2S. The stabilizer bottoms are separated into products and fractionator bottoms in the fractionator and the fractionator bottoms are recycled to the second reaction stage.

The approximate distribution of H_2S in the streams leaving the low-pressure separator is as follows:

Table 6. H_2S DISTRIBUTION IN THE LOW-PRESSURE SEPARATOR

Phase	Wt. % Feed Sulfur
Liquid	85
Vapor	15
Total	100

Pollution Sources

Point sources for possible pollutant emission in a hydrocracking unit are:

1. Sour water containing H_2S and NH_3 leaves the first stage high pressure separator, the low pressure separator, and the stabilizer accumulator. All these streams have to be treated in a sour water stripper before being discharged or reused (point 1 on Figure 18 and points 1 and 2 on Figure 19).

2. The bleed gas from the hydrogen rich gas in the first reaction stage may contain as much as 0.5 vol. % to 1.5 vol. % H_2S on Figure 18.

3. The catalyst is periodically regenerated in situ by burning off the accumulated coke (points 3 and 4 in Figure 18). (See Section BB, Catalyst Regeneration.)

4. Fuel gas produced in the distillation section contains H_2S

and needs to be treated. Points 3 and 4 on Figure 19.

5. Light ends produced in the distillation section contain some H_2S and need to be treated (point 5 on Figure 19).

L. HYDROGEN PRODUCTION

Hydrogen is an intermediate material in refining operations. It is used as a reactant in operations such as hydrogenation, hydrodesulfurization, and hydrocracking. The principal method for producing hydrogen is steam reforming of some available hydrocarbon like natural gas, refinery gas, propane, butane, or naphtha. Hydrogen is also produced in the refinery as a by-product in the reforming process.

The sequence of processing steps for hydrogen production by steam reforming is sulfur removal, reforming, shift conversion, carbon dioxide absorption in monoethanolamine (MEA) solution and methanation. The plant is in steam balance, that is, high-pressure steam for reforming and low-pressure steam for MEA regeneration and deaeration is produced as a by-product. The flow diagram is shown on Figure 20. The gas feed to the plant normally contains traces of sulfur which are removed by adsorption on activated carbon. Two carbon beds are used, normally operating in series flow. During regeneration, one bed is valved out of the normal flow and returned after regeneration to the downstream position in the flow sequence.

The sulfur-free gas is mixed with high-pressure steam and pre-heated in the convection section of the reformer furnace. The

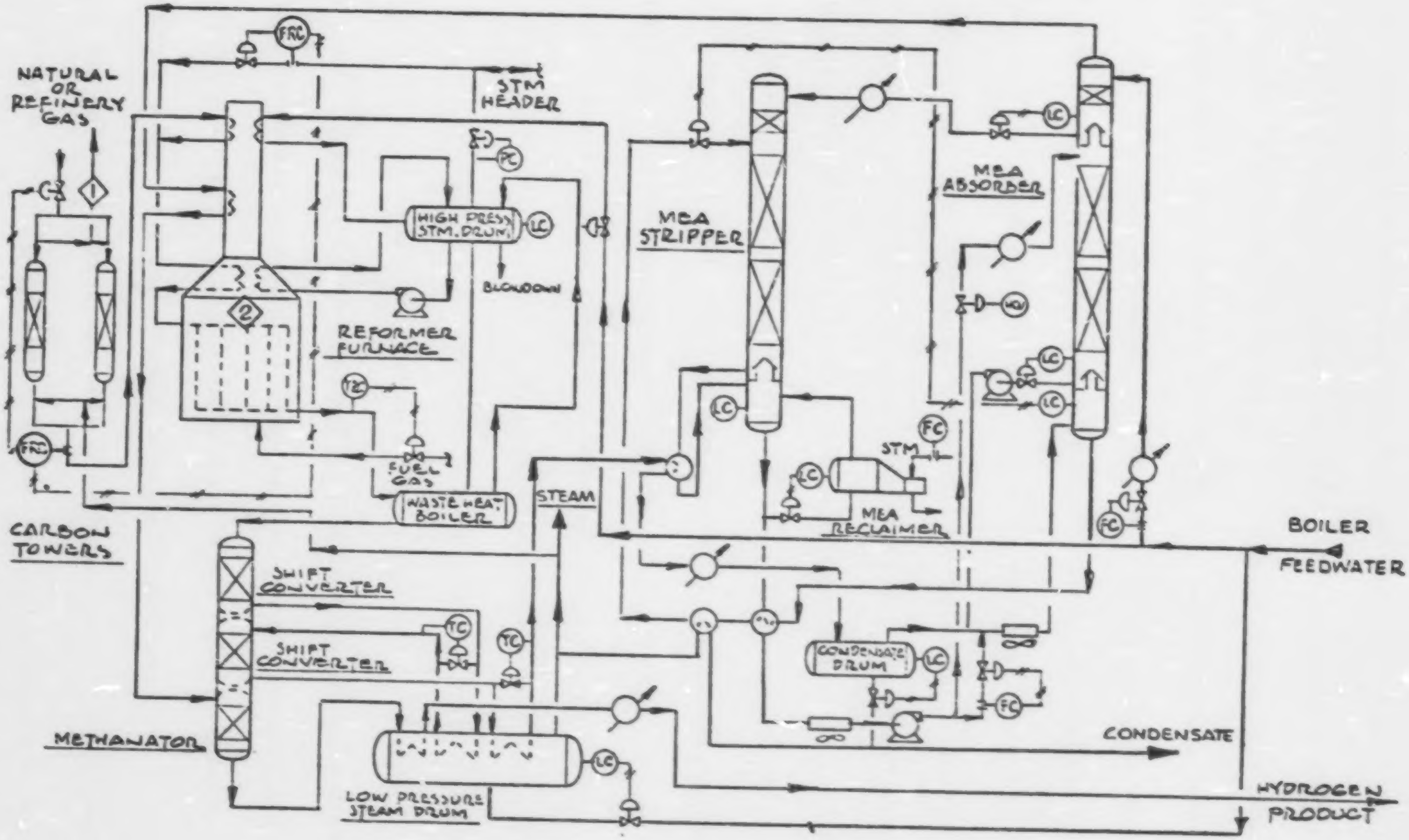

NATURAL OR REFINERY GAS
1
FRC
STM HEADER
2
HIGH PRESS. STM. DRUM
LC
PC
BLOWDOWN
REFORMER FURNACE
TRC
FUEL GAS
WASTE HEAT BOILER
CARBON TOWERS
STEAM
MEA STRIPPER
MEA ABSORBER
FC
STM
MEA RECLAIMER
BOILER FEEDWATER
SHIFT CONVERTER
SHIFT CONVERTER
TC
METHANATOR
LOW PRESSURE STEAM DRUM
CONDENSATE DRUM
CONDENSATE
HYDROGEN PRODUCT

Figure 20. Hydrogen production by steam reforming.

mixed gas flows downward through catalyst-filled tubes where steam reacts with methane and other hydrocarbons to produce hydrogen, carbon monoxide, and carbon dioxide. The high-temperature effluent gas from the reformer furnace flows through the tubeside of a steam generator producing high-pressure steam. Additional high-pressure steam is generated in the convection section of the furnace. This steam is consumed in the reforming reaction. More than three-quarters of the total hydrogen is produced in the reforming reaction. The remaining hydrogen is produced by the shift conversion of carbon monoxide to carbon dioxide. The catalytic conversion occurs in two stages, one at high temperature and the second at low temperature. The combination of converters shifts over 98 percent of the total carbon oxides to carbon dioxide and hydrogen. Reaction heat is removed between the two stages of shift conversion by generating low pressure steam. The gas temperature between the catalyst beds is also lowered to give more favorable conditions for the shift reaction.

The crude hydrogen gas from the shift converter is further cooled before mixing with MEA solution in an exchanger. The heat of reaction between carbon dioxide and MEA is largely removed in this precontact stage ahead of the amine absorber. The remaining carbon dioxide is removed from the gas stream by reaction in the absorber. The heat for MEA regeneration is supplied partly from the process gas and partly from low pressure steam. An MEA reclaimer is provided to maintain a clean active solution. Other means of absorbing carbon dioxide may be used instead of MEA; these include Sulfinol and activated hot carbonate.

The last traces of carbon monoxide and carbon dioxide are converted to methane by reaction with hydrogen in the methanator. This catalytic reaction requires a preheat temperature of about 600°F. The residual carbon oxide content of the product hydrogen is less than 10 ppm.

Pollution Sources

There are two potential sources of pollution in the steam reforming process. During carbon tower regeneration (point 1 in the figure), H_2S and organic sulfur compounds are removed using steam. This steam should be condensed and transferred to the sour water system for processing.

The periodic replacement of catalyst beds could result in pollution if the removed catalyst is allowed to weather in an open area (point 2). The spent catalyst should be put in containers when removed from process equipment and disposed of in an acceptable manner.

M. SWEETENING

A distillate is said to be sour if it contains noticeable amounts of sulfur compounds, particularly the odoriferous mercaptans. A process that removes these compounds or converts them to less objectionable forms is called "sweetening". Hydrotreating, which could be called a sweetening process is discussed in Section I.

Sweetening can be accomplished by removing the mercaptan, usually by extraction or by converting it to a disulfide. Frequently, the solutions used for extraction are regenerated by converting the mercaptans in them to disulfides and then removing the disulfides. In treating light distillates or light naphtha, lighter mercaptans can be satisfactorily removed by extraction with caustic solutions containing solubility promotors. The high molecular weight mercaptans associated with the heavier distillates, such as full-range gasoline or kerosene, are more difficult to extract and are normally converted to disulfides and left in the distillate.

Doctor sweetening, copper sweetening, and hypochlorite sweetening are old processes and are not in general use at this time. In doctor sweetening, the distillate is treated with alkaline sodium plumbite solution to oxidize the mercaptan to disulfide. The lead is reduced to lead sulfide and is discarded or regenerated by air blowing. In copper sweetening, cupric chloride is reduced to cuprous chloride, followed by regeneration with air to recover the cupric chloride. In hypochlorite sweetening, sodium or calcium hypochlorite is used as the oxidizing agent without regeneration.

There is a variety of sweetening processes in use today, for instance, treatment with sulfuric acid or absorbing mercaptan with molecular sieves. However, the more widely used processes usually employ sodium hydroxide with added catalysts or promoters. Most frequently a caustic solution containing the dissolved catalyst or promoter is employed, but a fixed bed of catalyst can also be used.

Figure 21 is a flow diagram for a gasoline-sweetening process that employs a sodium hydroxide solution (caustic) containing a dissolved catalyst. Sour gasoline feed is metered into the extractor, where it is brought into contact with recycled regenerated caustic solution. Partially treated gasoline, with part of the mercaptan removed, flows from the top of the extractor and is mixed with recycled caustic solution and air before entering the bottom of the sweetener. The remaining mercaptan is oxidized to disulfide in the sweetener and remains in the treated gasoline stream. Caustic solution is separated from the treated gasoline in the solution settler and is recycled to the sweetener. Caustic solution from the extractor, containing dissolved mercaptan, is mixed with air and sent to the oxidizer. The mercaptan is oxidized to disulfide in the oxidizer and then flows to the air separator. Excess air is vented from the air separator, and the caustic solution and disulfide flow to the disulfide separator. The insoluble disulfide layer separates and is withdrawn from the system, and the regenerated caustic is recycled to the extractor.

Pollution Sources

There are two points of possible pollutant emission of special interest in the process. One is the disulfide product stream (point 1 in the figure). If the disulfide cannot be sold, it will normally be disposed of by burning as fuel or by incineration. Since the stream is small,

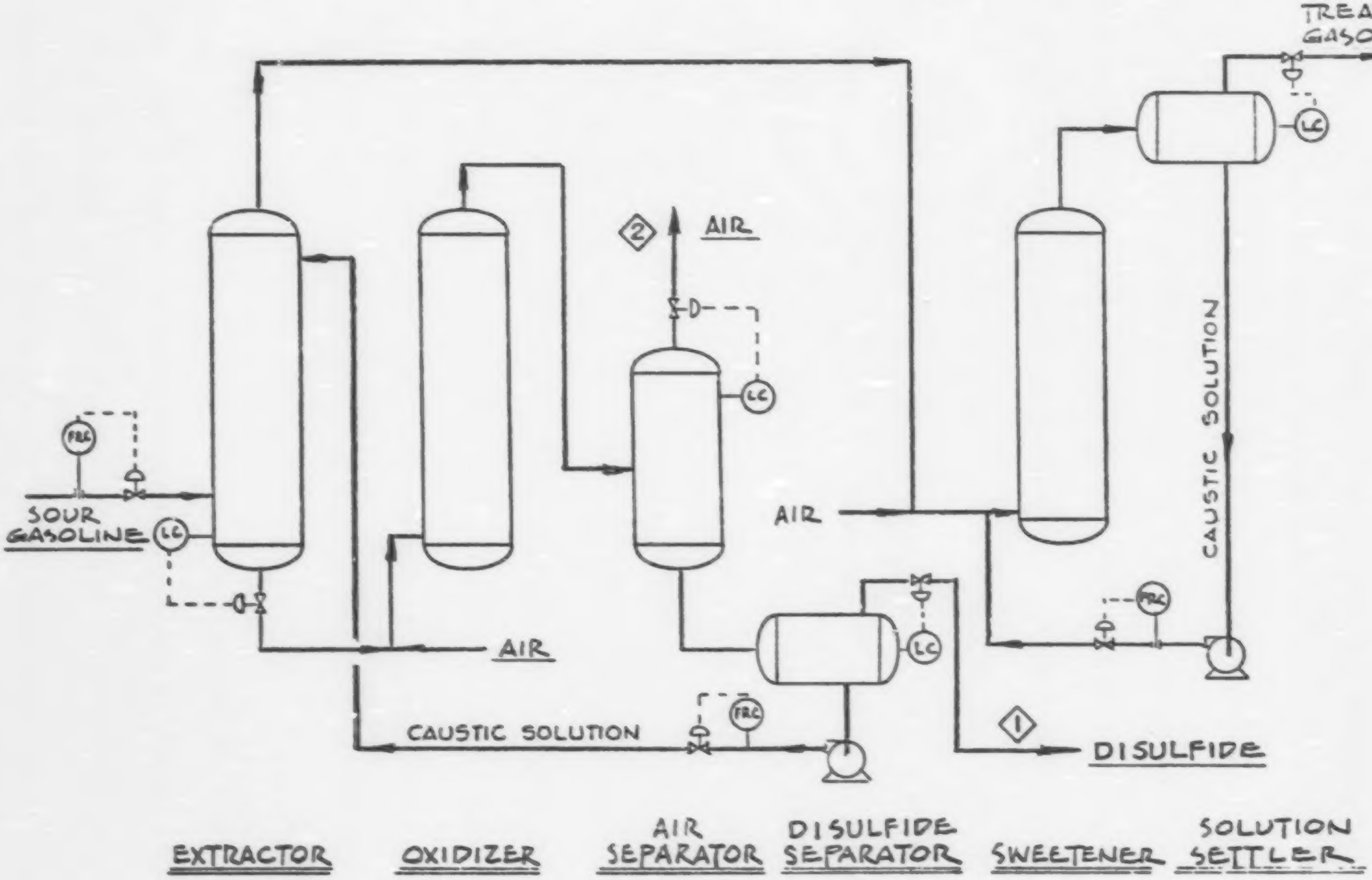

TREATED GASOLINE
LC
2
AIR
LC
FRC
SOUR GASOLINE
LC
AIR
CAUSTIC SOLUTION
AIR
CAUSTIC SOLUTION
FRC
LC
FRC
1
DISULFIDE
EXTRACTOR
OXIDIZER
AIR SEPARATOR
DISULFIDE SEPARATOR
SWEETENER
SOLUTION SETTLER

Figure 21. Gasoline sweetening.

this may be permissible, but in some cases it may be necessary to use an incinerator equipped for sulfur dioxide recovery. Incinerator emissions may be the subject of future control regulations. The other pollution emission is the excess air from the air separator (point 2). Since this air will contain disulfide, it may be necessary to incinerate it.

N. ASPHALT AIR BLOWING

Asphalt used for composition roofing and shingles is usually blown with air to oxidize the material. The oxidation reaction increases the hardness and raises the melting point of the asphaltic material and improves its resistance to weathering. In some processes a catalyst such as ferric chloride or phosphorous pentoxide is added to the asphalt to produce a product with a very high melting point and hardness.

Figure 22 is a typical schematic diagram of an air-blowing asphalt-treating facility. The feed to the asphalt plant will usually be a residuum from a vacuum distillation of a topped crude. The reaction is usually carried out in a batch operation. The feed is preheated to 400 to 600°F in a fired heater and then pumped into the reactor. The reactor is usually a vertical vessel which is partially filled with feed stock. Air is compressed to a pressure high enough to permit discharging it into the residuum through a sparger at the base of the reactor. As the gases rise through the liquid, an exothermal reaction takes place between the oxygen and the hydrogen in the oil. Simultaneous chemical reactions cause polymerization and formation of oxygen

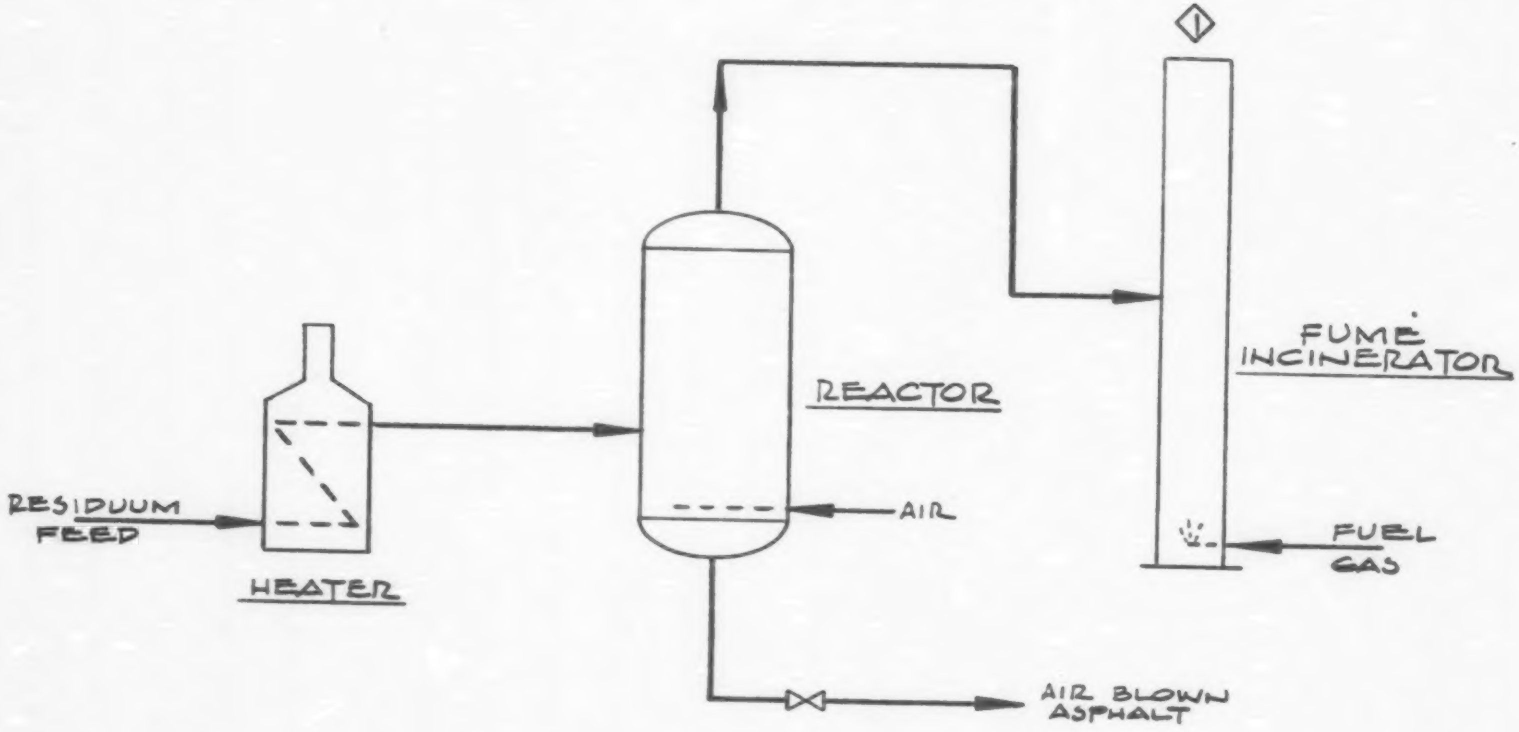

FUME INCINERATOR
REACTOR
RESIDUUM FEED
HEATER
AIR
FUEL GAS
AIR BLOWN ASPHALT

Figure 22. Asphalt air blowing.

linkages. The blowing reaction may be continued for periods of from one to 24 hours.

Pollution Sources

The gases which are vented from the reactor contain hydrocarbon vapors and aerosol particles of oil. These gases used to constitute one of the major forms of air pollution from a refinery. Now the vent gases are normally incinerated which eliminates the objectionable constituents in the vent gas. However, the incinerator remains a potential source of air pollution (point 1 on the figure).

O. ACID GAS TREATING

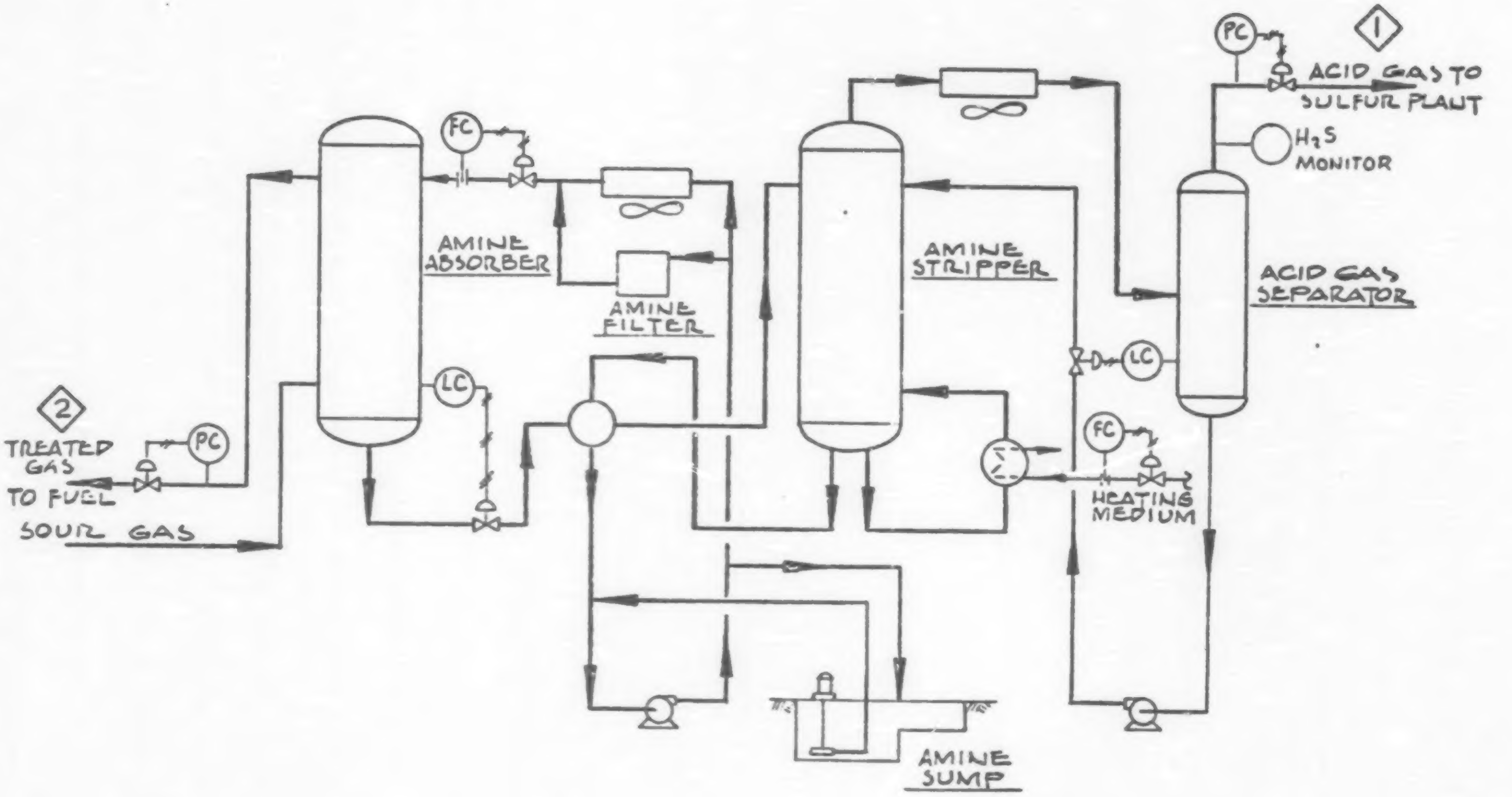
Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are called acid gases, and a gas stream containing H_2S is called sour gas. Since sour gas is produced in a number of processes during normal refinery operation, untreated refinery fuel gas can be expected to be sour. It is generally necessary to treat the gas for H_2S removal before it is used as refinery fuel. This is done to avoid the air pollution that results from the sulfur dioxide (SO_2) formed in burning the H_2S.

Acid gases are removed by absorbing them in an alkaline solution. The alkaline material, monoethanolamine for instance, is chosen so that the chemical bond formed during absorption can be broken by heating. The acid gas is stripped from the heated solution and the solution, after cooling, is ready for reuse. Solution containing acid gas is called "rich" and the regenerated solution is called "lean".

Several acid gas treating processes are available but the differences are primarily in the choice of alkaline absorbent. The processes are similar in that the acid gas is absorbed in the alkaline solution under pressure, and the solution is regenerated by heating at a low pressure.

1. Acid Gas Absorption Processes

a. Absorption in Monoethanolamine (MEA).- The absorbing medium is a 10 to 20 weight percent solution of MEA in water. Figure 23 shows the process flow for a typical MEA absorption system. Acid gas is removed from the sour gas by contacting with the MEA solution in the absorber. Sour gas enters the bottom of the column and cool, lean amine enters at the top. Treated gas leaves the top of the absorber and passes to the refinery fuel gas system. Rich amine, containing the absorbed acid gas, is used to cool the lean amine and is fed to the top of the stripper. Steam used for stripping the rich amine is generated by boiling the stripper bottoms in the reboiler. Acid gas and steam leave the top of the column and steam is condensed. Condensate and acid gas are separated in the acid gas separator and the condensate is pumped to the stripper as reflux. The acid gas flows to the sulfur plant for conversion to elemental sulfur. This stream is a potential source of air pollution (point 1 in the figure). Hot lean amine from the stripper reboiler is cooled and filtered before returning to the absorber.



1
PC
ACID GAS TO SULFUR PLANT
H₂S MONITOR
FC
AMINE ABSORBER
AMINE FILTER
AMINE STRIPPER
ACID GAS SEPARATOR
LC
2
TREATED GAS
TO FUEL
PC
LC
SOUR GAS
FC
HEATING MEDIUM
AMINE SUMP

Figure 23. Acid gas treating.

b. Absorption in Diethanolamine (DEA) - The absorbing medium is a 20 to 30 weight percent solution of DEA in water. The process flow scheme is identical to that shown for MEA in the figure.

c. Absorption in Hot Carbonate - The absorbing medium is a 15 to 30 weight percent solution of potassium carbonate in water. There are a number of variations to this process employing additives to improve solution performance. The major equipment and process flow are again similar to the MEA process.

The treated gas (point 2 in the figure) may be a source of air pollution if H_2S removal is incomplete. The H_2S content of this stream should be checked periodically, if not monitored continuously.

P. SULFUR RECOVERY

1. Process Objective

The sulfur recovery process, also known as the Claus process, is used to convert hydrogen sulfide to elemental sulfur. The feed stream contains acid gases (CO_2 and H_2S) obtained from the acid-gas recovery plant, but hydrocarbon impurities may also be present. The sulfur plant is normally designed to convert 90 to 95% of the H_2S to elemental sulfur, which requires two or three reaction stages, with the unrecovered sulfur being burned to SO_2 and vented to the atmosphere. However, recently implemented pollution regulations have, in some areas, required higher degrees of recovery. Tail gas cleanup processes have been developed for this purpose that reduce the SO_2 emissions from the sulfur plants.

2. Process Description

Hydrogen sulfide is converted to elemental sulfur in two steps. In the first step, H_2S is partially burned to SO_2 with air. The H_2S/SO_2 mixture is then reacted over a catalyst to produce sulfur and water. This reaction is known as the shift conversion and is carried out in two or three stages with sulfur removal after each stage. The design of a sulfur recovery plant depends upon the acid gas composition. If the concentration of H_2S in the feed is high, a "straight-through" process is used. In the straight-through configuration, all of the acid gas and air are fed to the burner. If the H_2S concentration in the feed is low, a "split-flow" or "sulfur recycle" process is used. In the "split-flow" process, a portion of the feed is burned completely to SO_2 and combined with the remainder of the feed to provide the proper H_2S/SO_2 ratio for the shift conversion. In the "sulfur recycle" process, the product sulfur is recycled to the burner to support combustion. A fourth type of sulfur recovery process uses the "direct oxidation" approach. This configuration, which is for very lean feeds, eliminates the burner by feeding the acid gas/air mixture directly to a catalytic burner.

Most sulfur plants in refineries are the "straight-through" or "split-flow" type. A flow diagram for a typical refinery sulfur recovery process is shown in Figure 24. The acid-gas stream containing H_2S,

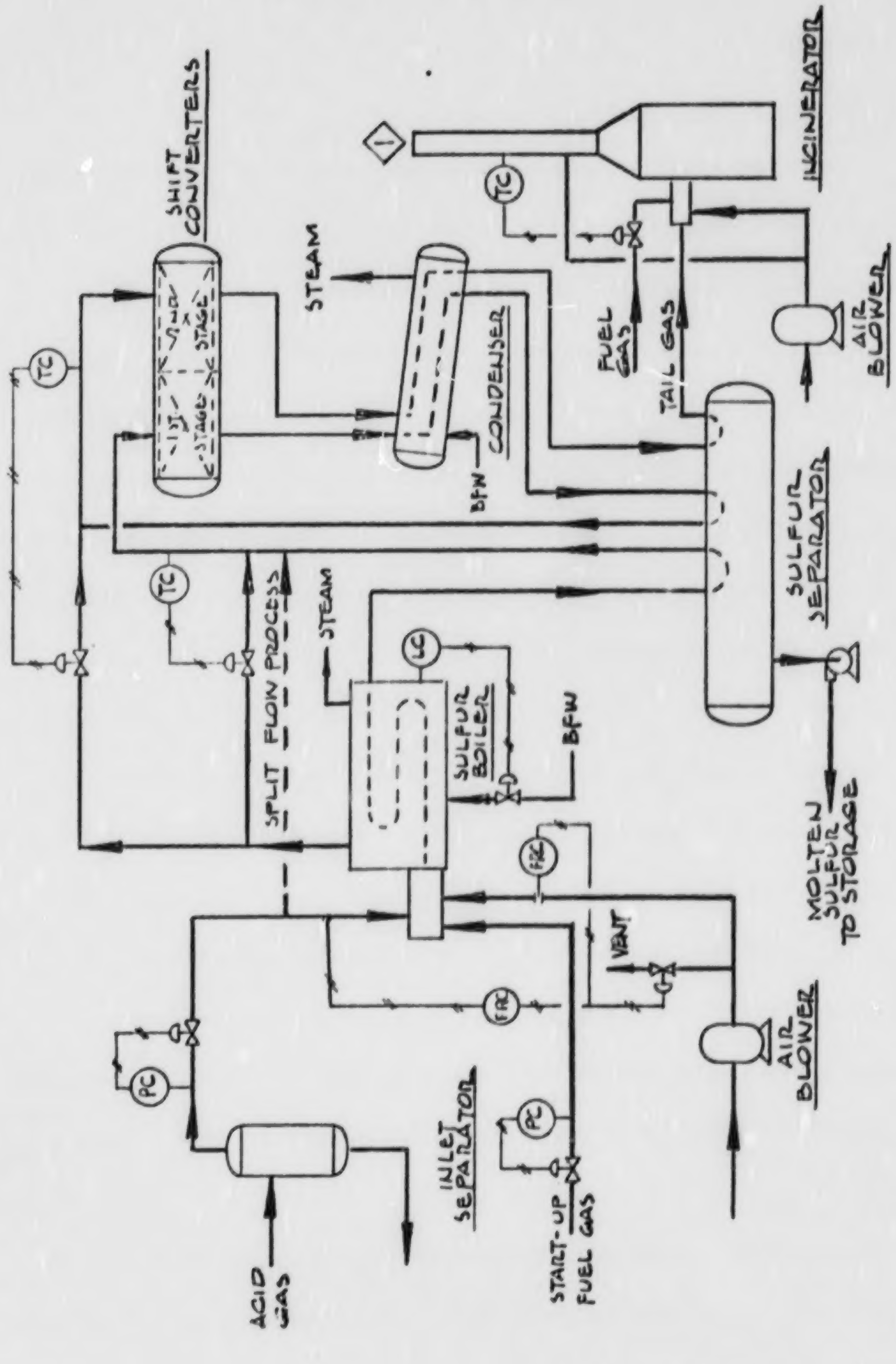

ACID GAS
INLET SEPARATOR
PC
START-UP FUEL GAS
PC
AIR BLOWER
VENT
FRC
FRC
SPLIT FLOW PROCESS
TC
TC
STEAM
LC
SULFUR BOILER
BFW
SHIFT CONVERTERS
1st STAGE
2nd STAGE
STEAM
CONDENSER
BFW
SULFUR SEPARATOR
MOLTEN SULFUR TO STORAGE
TAIL GAS
FUEL GAS
AIR BLOWER
TC
1
INCINERATOR

Figure 24. Sulfur Plant.

CO_2, water, and minor amounts of hydrocarbons is fed to an inlet separator where any entrained liquid is removed. The acid gas and air are fed to the sulfur boiler. Fuel gas lines are provided to assist in plant startup. Boiler feed water is fed to the sulfur boiler to generate low-pressure steam. The sulfur boiler usually contains three tube passes. A portion of the gases is diverted from the boiler after two passes to provide preheat for the shift converter feeds. In some plants an auxiliary burner is provided to furnish preheat to the reactors. Liquid sulfur is separated from the boiler effluent gases and is sent to the sulfur pit for storage. The gases are mixed with the reheat stream and fed to the first-stage shift converter. The effluent from the reactor is passed through the condenser. Sulfur is separated and sent to the sulfur pit and the gases are fed to the second-stage converter. Approximately 5% of the sulfur fed remains in the tail gas. This sulfur is converted to SO_2 in the tail-gas incinerator.

In some sulfur plants, the sulfur boiler and condenser are combined into a single unit. The catalytic converters are often combined into a single horizontal or vertical vessel. Combining the units in this manner permits many smaller plants to be shop fabricated and skid-mounted.

3. Instrumentation

The acid-gas feed to the sulfur plant is on pressure control. The plant is designed to accept acid-gas flows as they develop in the refinery and a plant may be designed to operate at 25% of capacity to allow for future demand. The ratio of acid gas to air is controlled by a special ratio flow controller. To set the proper ratio, the acid gas must be analyzed regularly to determine the H_2S concentration. The proper H_2S/air ratio is critical to the operation of the plant since the concentration of SO_2 in the incinerator stack gases will increase if the improper ratio is set. Automatic stream analyzers can be used to set the proper ratio on a nearly continuous basis. The volume of reheat streams is controlled to set the inlet temperatures to the shift converters. If these temperatures are allowed to fall, the reaction will be incomplete and sulfur recovery will drop. Incinerator stack temperature is controlled by setting fuel consumption and air bypass. A high temperature is required to ensure complete combustion of sulfur compounds to SO_2 and good dispersal of gas to the atmosphere.

4. Pollution Sources

The stack gas emissions (point 1 in the figure) are the major source of pollution from sulfur plants. The concentration of SO_2 in the stack gas will depend on the number of stages, feed gas composition, operating efficiency, amount of dilution air and plant upsets. In a typical plant with two reactor stages, the stack gas will contain up to 10% of the feed sulfur. The presence of hydrocarbons in the feed will be detrimental to sulfur recovery and pollutant emissions. Some of the hydrocarbons are converted to carbon disulfide and carbonyl sulfide in the burner. These compounds are essentially inert and pass through to the incinerator where they are emitted as SO_2. Hydrocarbons can also foul the shift conversion catalyst and reduce sulfur recovery.

5. Tail-Gas Treatment Processes

Tighter air pollution regulations have forced many sulfur plant operations to consider "hang-on" plants to reduce SO_2 emissions. Numerous processes have been developed to treat sulfur plant tail gas. The more important tail-gas treating processes are discussed below.

a. Modified Stretford Process - The Stretford Process has been used in Great Britain for many years to recover hydrogen sulfide from natural gas and convert it to sulfur. The feed gas is passed through an absorption tower which removes the H_2S. The absorbent is an organic liquid which also serves to oxidize the dissolved H_2S to sulfur. The sulfur is removed from the liquid by filtration, and the solvent is regenerated by air oxidation. Very high conversions of H_2S to sulfur are possible with this process.

Since the Stretford Process is not suitable for use with feed gases containing SO_2, two modified versions have been developed for use with sulfur plant tail gas. The Beavon Process uses a small catalytic reactor to hydrogenate the SO_2, COS, and CS_2 to H_2S before feeding the gas to a Stretford tower. The Cleanair Process hydrolyzes the impurities to H_2S and SO_2. The gas is then cooled to permit the Claus reaction to take place. At low temperatures the conversion of SO_2 to sulfur is complete and the remaining H_2S is fed to a Stretford Tower. Adding a

Modified Stretford unit can reduce the incinerator stack concentration of SO_2 to 250 ppm.

b. Solution Claus Process - The Claus reaction between H_2S and SO_2 has a higher sulfur yield at low temperatures. In the IFP Process (developed by the Institut Francais de Petrole) H_2S and SO_2 react in stoichiometric amounts in a liquid-phase solvent. The temperature is kept above the melting point of sulfur so that molten sulfur can be drained from the bottom of the tower. The solvent is cooled and recycled to the tower. Treated gas is incinerated as in other processes. The IFP Process can reduce SO_2 in the stack gas to 2, 000 ppm.

c. Sulfreen Process - This process uses a low-temperature Claus reaction on an activated carbon catalyst. The sulfur produced is adsorbed on the carbon and is removed by stripping with inert gas in a second step. Reduction of SO_2 in the stack gas is comparable to that of the IFP Process.

d. Stack-Gas Treating Processes - Another approach to reducing stack-gas emissions is to treat the stack gas rather than the tail gas. Several schemes have been proposed to remove or recover SO_2 from stack gases. One such process that has received some attention is the Wellman-SO_2 Recovery Process. The stack gases are cooled and fed to a tower where SO_2 is absorbed in sodium sulfite solution to form sodium bisulfite. The sodium bisulfite is heated to drive off the SO_2 and the sulfite is crystallized, redissolved, and recycled to the tower. The SO_2 is recycled to the sulfur plant. Effluent gas concentrations may be reduced to 100 ppm SO_2.

Q. SOUR WATER STRIPPING

Water containing sulfides is called sour water. Refinery operations produce sour water from processes such as steam stripping and whenever steam is condensed in the presence of gases containing hydrogen sulfide. Sour water may also contain ammonia and phenols. Steam stripping has been used by refineries to reduce the level of contaminants in sour condensate to allow either further use of this condensate or its return to public waters. There are two types of sour water steam strippers: refluxed and nonrefluxed.

1. Refluxed Sour Water Steam Strippers

Figure 25 shows the process flow for a typical refluxed stripper. Sour water feed may be flashed to release some vapor and then stored in a surge tank. The sour water is then pumped through a preheat exchanger and into the top of the stripper column. Steam is fed into the bottom of the column. Sour gas, containing steam and contaminants, leaves the top of the stripper and is partially condensed. Condensate and sour gas are separated in the surge tank and the condensate is recycled to the stripper. The sour gas is disposed of either by conversion to sulfur in a sulfur plant or by incineration, where air pollution control regulations allow the emission of the sulfur dioxide resulting

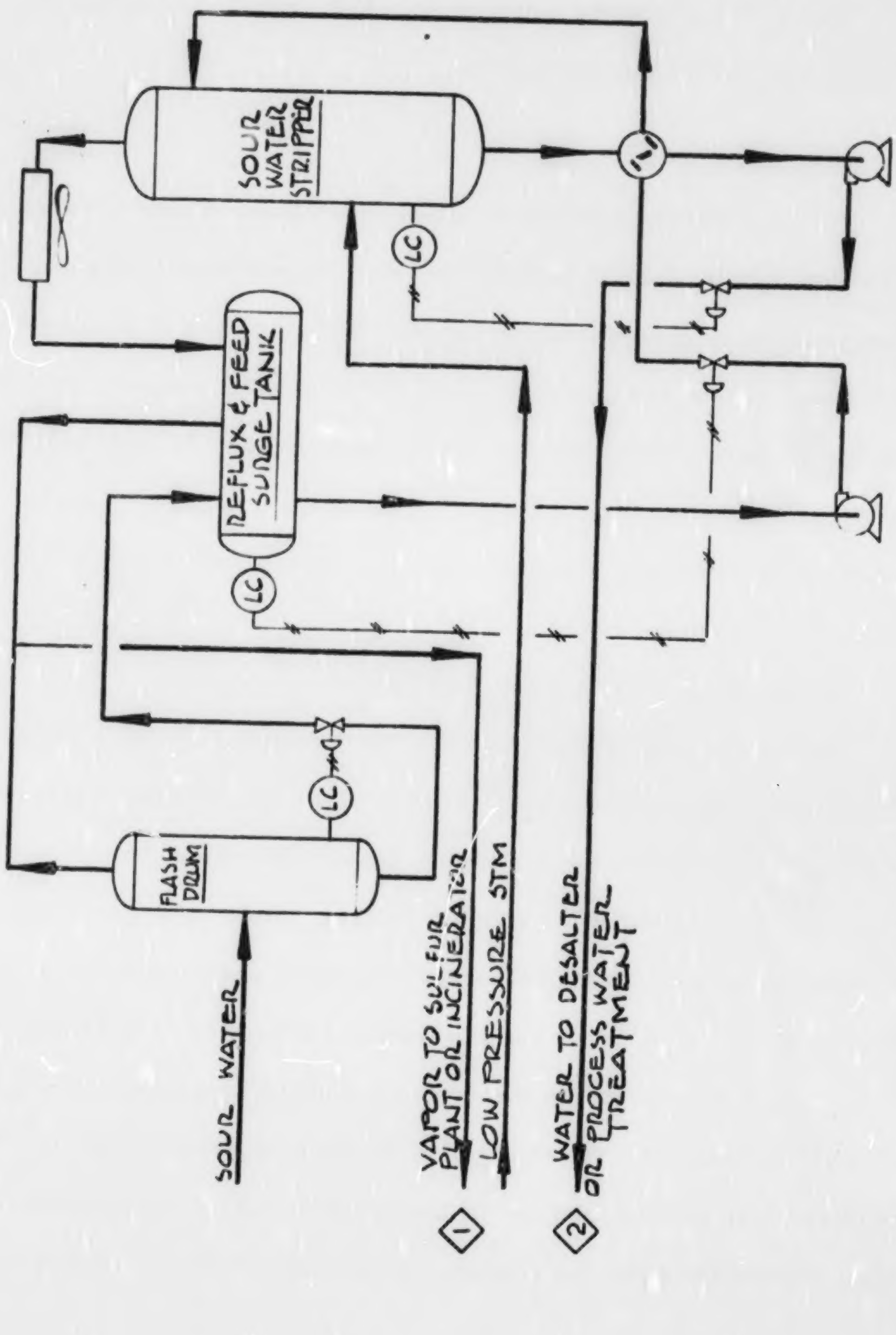

SOUR WATER
FLASH DRUM
LC
REFLUX & FEED SURGE TANK
LC
SOUR WATER STRIPPER
LC
1
VAPOR TO SULFUR PLANT OR INCINERATOR
LOW PRESSURE STM
2
WATER TO DESALTER OR PROCESS WATER TREATMENT

Figure 25. Sour water stripping process.

from incineration. The stripped water is removed from the bottom of the column and either is used as a process water stream or flows to the waste water treatment system.

The pollution potential of the sour gas stream (point 1 in the figure) is apparent because of its H_2S content. Further processing of this stream is necessary before emission to the atmosphere. The stripped water (point 2) may be a source of odor problems if traces of dissolved H_2S remain and the stream flows to an open waste water treatment system.

2. Nonrefluxed Sour Water Steam Strippers

In these systems there is no overhead condensing system and the column overhead goes directly to either flare or incineration. This stream has proved hard to dispose of because of the large volume of steam and is a potential source of pollution.

R. NATURAL GAS PROCESSING

Natural gas processing refers to processes used to remove impurities and to recover heavier hydrocarbons from natural gas.

Natural gas is a mixture of methane and ethane that occurs in nature as deposits trapped in geologic structures. The gas may occur in combination with crude oil or alone and at pressures varying from hundreds of pounds per square inch to substantial vacuums. Usually water or brine is produced along with the gas, and the gas can be expected to contain nonhydrocarbon impurities and heavier hydrocarbons.

Water, brine, and crude oil where present are usually separated from the gas at the production location. The field separators or gas traps, used for this purpose, are simple physical separation devices. The separated gas can be expected to be saturated with water vapor and will frequently contain heavier hydrocarbon vapors, carbon dioxide and hydrogen sulfide.

Mixtures of water vapor and natural gas, at elevated pressures and low temperatures, can form gas hydrates. These icelike solids plug lines and otherwise interfere with transport and storage equipment. Water vapor, carbon dioxide, and hydrogen sulfide are corrosive and hydrogen sulfide is a potential air pollutant. For these reasons it is frequently desirable to remove such impurities from natural gas.

The heavier hydrocarbon vapors are often separated to recover LPG and natural gasoline which are valuable products. LPG is propane, butane, or mixtures of both. Natural gasoline is a component of motor gasoline consisting of mixtures of butanes, pentanes, hexanes, and lesser amounts of still heavier hydrocarbons.

1. Gas Dehydration Using Liquid Absorbent

Natural gas is dehydrated by using either absorption in a hygroscopic liquid or adsorption on a solid desiccant. In processes employing liquid absorbents, the liquid is continuously regenerated and recycled. Solid adsorbents are usually regenerated periodically, with two or more vessels used to provide continuous operation.

Diethylene glycol, triethylene glycol, and calcium chloride brine are commonly used liquid absorbents. The glycol dehydration process which is typical of the processes using absorbents is shown in Figure 26. Gas is brought into the system through an inlet scrubber to remove any entrained liquid water or hydrocarbon. The gas is then dried by countercurrent contact with the absorbent in the absorber. Dehydrated gas leaves the system from the top of the absorber and the absorbent containing water leaves from the bottom. Since the absorber is normally operated at pressures of several hundred pounds per square inch, some gas will be dissolved in the absorbent. This gas is separated in a flash vessel at reduced pressure and delivered to the fuel gas system. The absorption liquid is then fed to a distillation column, or still, for regeneration. Water is distilled overhead, along with a minor amount of gas which is sent to the flare. The regenerated absorbent is recycled to the absorber after cooling by exchange with the feed stream and cooling water.

Water from the inlet scrubber (point 1 in the figure) and the still overhead (point 2) may contain sulfides. If so, these streams should be routed to a sour water stripping system. Flash tank gas (point 3) may contain hydrogen sulfide and may require treatment before being used for fuel.

2. Gas Dehydration Using Solid Adsorbent

Alumina, silica gel, and molecular sieves are three commonly used solid adsorbents. Figure 27 is a flow sheet for a typical adsorbent

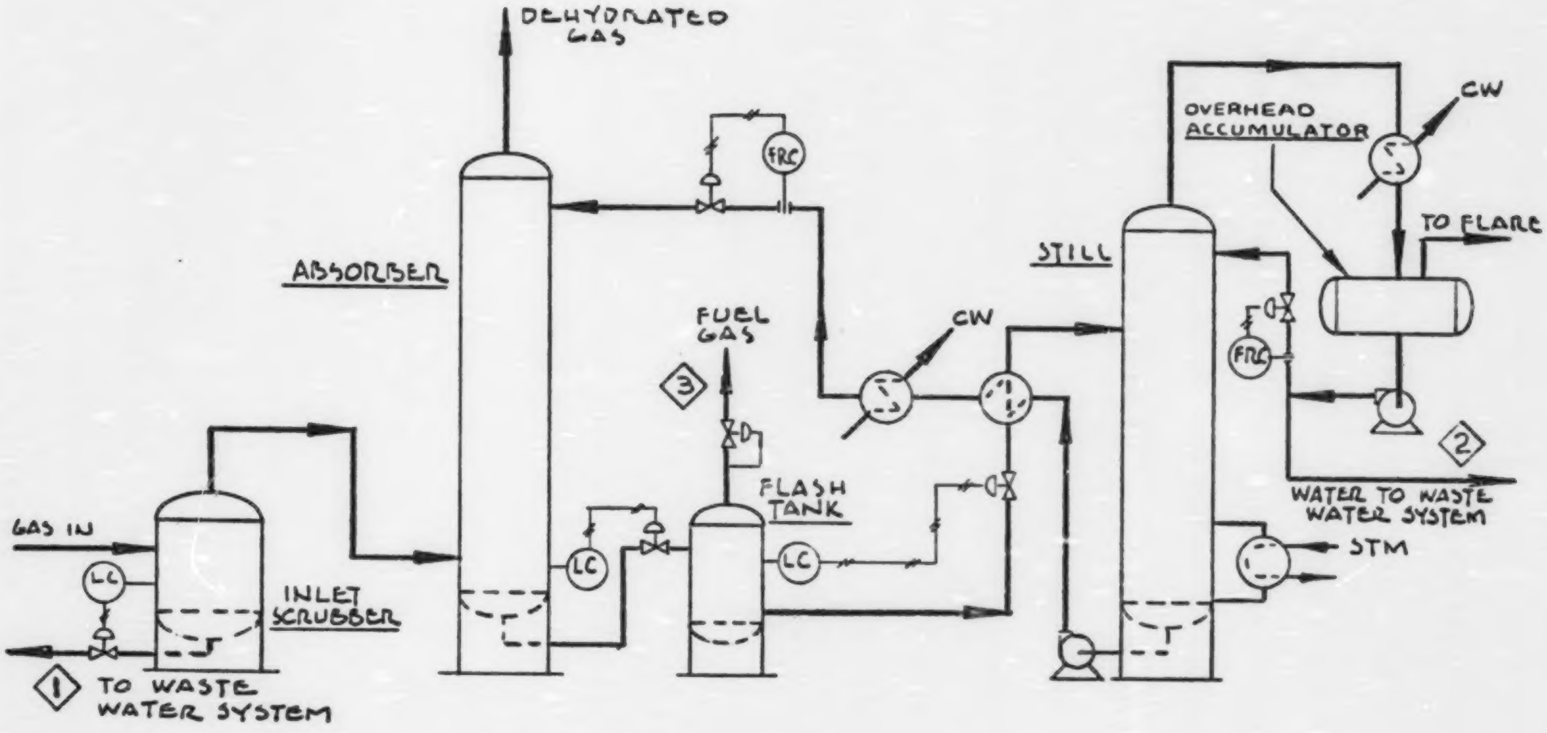

DEHYDRATED GAS
ABSORBER
FRC
FUEL GAS
3
CW
STILL
OVERHEAD ACCUMULATOR
CW
TO FLARE
FRC
2
WATER TO WASTE WATER SYSTEM
STM
GAS IN
LC
INLET SCRUBBER
LC
FLASH TANK
LC
1
TO WASTE WATER SYSTEM

Figure 26. Glycol dehydration.

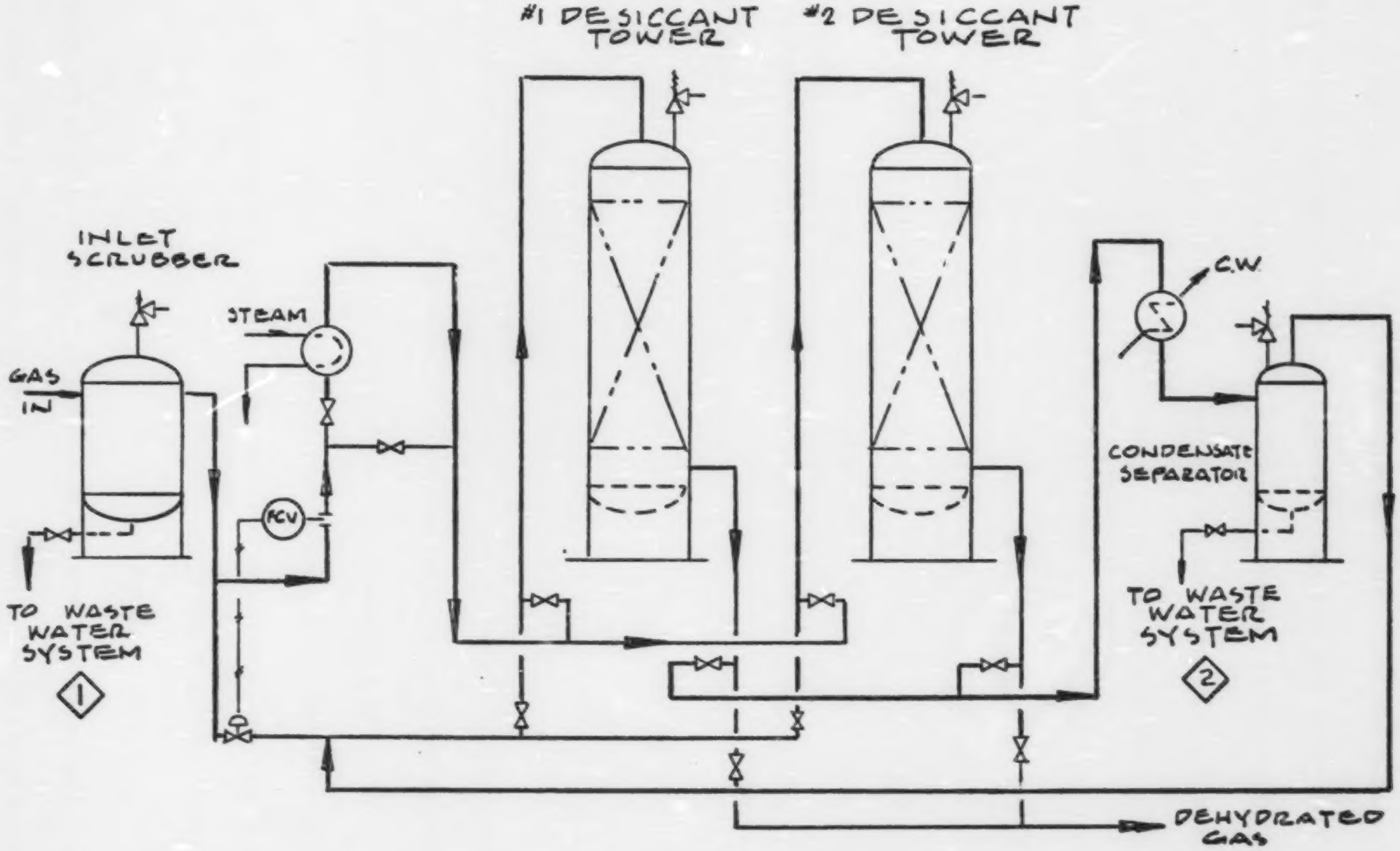

#1 DESICCANT TOWER
#2 DESICCANT TOWER
INLET SCRUBBER
STEAM
GAS IN
FCV
C.W.
CONDENSATE SEPARATOR
TO WASTE WATER SYSTEM
1
TO WASTE WATER SYSTEM
2
DEHYDRATED GAS

Figure 27. Adsorbent dehydration.

dehydration process. Since the adsorbent is regenerated in place, two dehydration vessels are provided to permit continuous operation. One vessel is in service while the other is being regenerated. In the following description, it is assumed that one desiccant tower is in service while the other tower is being regenerated. Gas is brought into the system through an inlet scrubber to remove any entrained liquid water. The main flow, to the # 1 desiccant tower, is controlled by a flow-control valve taking its signal from a flow sensor in the bypass used for regeneration. Gas flows downward through the tower and dehydrated gas leaves the process from the bottom of the tower.

The # 2 desiccant tower is regenerated while the # 1 tower is on stream. A bypass stream from the main gas flow is heated and then passed through the # 2 tower. Gas and water vapor from the tower are cooled to condense the water. The water is separated from the gas in the condensate separator and the gas is returned to the main gas stream. After regeneration, the desiccant bed is cooled by bypassing the heater and passing cool gas through the tower.

Depending on the pressure of operation and on the amount of hydrogen sulfide in the gas, it may be desirable to treat the water removed from the process to control dissolved hydrocarbon and sulfide emissions (points 1 and 2).

3. Acid Gas Removal

The processes applied to natural gas are essentially the same as those covered under Section O, Acid Gas Treating. There are, however, some differences attributable to the usually much higher pressures of the gas to be treated.

Glycol is often added to the amine in an amine process to provide simultaneous dehydration and acid gas removal.

In amine plants, a flash tank and reabsorber are normally added to the rich amine circuit between the absorber and the stripper. This arrangement is shown in Figure 28. Natural gas absorbed at the high absorber pressures is released at a lower pressure in the flash tank. Since the flashed gas is sour, a small reabsorber column is mounted on the flash tank. A slip stream of lean amine is fed to the reabsorber to remove the acid gas from the flashed gas before the gas is sent to the fuel gas system.

Since the absorber pressure is much higher than the stripper pressure, a large amount of power is required to pump lean treating solution from the stripper to the absorber. Some of this power can be supplied by utilizing the pressure difference available in the rich solution circuit. A pressure breakdown turbine is inserted in the rich solution circuit and the turbine is used to drive the lean solution pump. A motor or steam turbine is used to supply the balance of the power required.

4. LPG and Natural Gasoline Recovery by Compression

Natural gas is often transported through high pressure pipelines as a matter of economy. Where the gas is produced at low pressure, the gas must first be compressed. Although natural gas is seldom

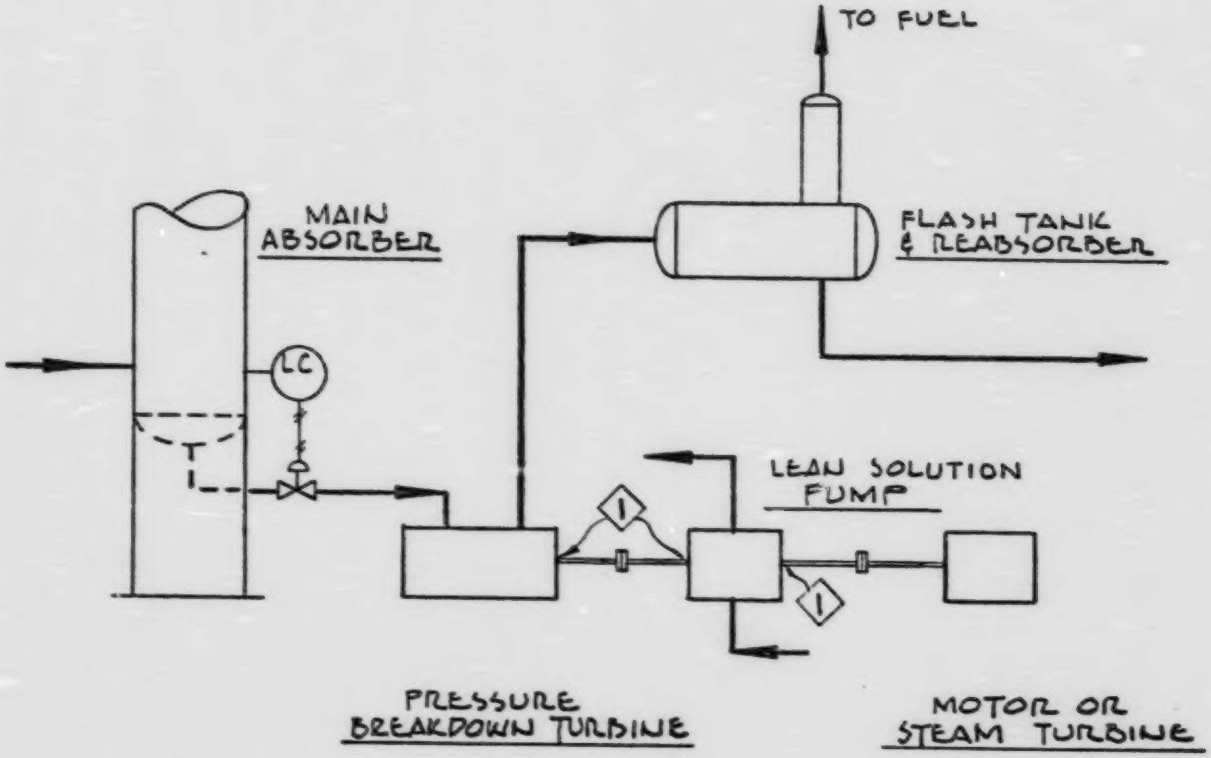

TO FUEL
MAIN ABSORBER
FLASH TANK & REABSORBER
LC
1
1
LEAN SOLUTION PUMP
PRESSURE BREAKDOWN TURBINE
MOTOR OR STEAM TURBINE

Figure 28. Amine-water and glycol amine process using breakdown turbine.

compressed solely for the purpose of LPG or natural gasoline recovery, significant amounts of these products are recovered from compressor stations. Under pressure, the heavy hydrocarbons are condensed and separated from the natural gas. Since the increase in pressure per stage, expressed as the ratio of outlet to inlet pressure, is limited by practical considerations, several stages of compression may be needed to reach the required pressure.

Figure 29 is a flow sheet for a typical two-stage compressor station. Gas enters through an inlet scrubber or knock out drum to remove entrained liquid. The gas is compressed in the first stage cylinder, cooled by a cooling water exchanger and sent to the first stage accumulator. Water and hydrocarbon are separated from the gas under liquid level and interface level control. The hydrocarbon is sent to a distillation unit for recovery of LPG and natural gasoline (see Section S, Light Ends Recovery). The gas is then compressed in the second stage in a similar manner. The first and second stage cylinders are usually driven by a single engine or motor.

The water streams (points 1, 2, and 3 in the figure) may contain sulfides and hydrocarbons. If so, they should be routed to separators and a sour water stripper.

5. LPG and Natural Gasoline Recovery by Refrigeration

The amount of heavy hydrocarbon vapor that can be held at saturation by natural gas decreases with decreasing temperature or increasing pressure. Increased recovery of LPG and natural gasoline can be

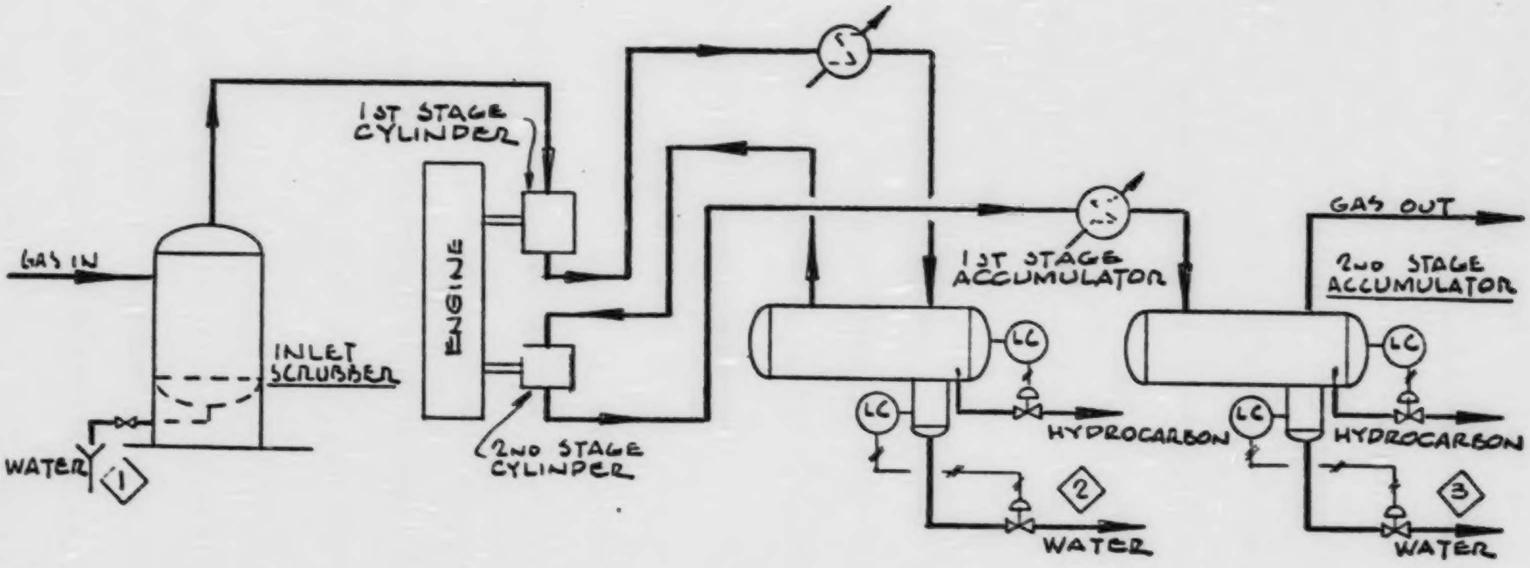

GAS IN
WATER
1
INLET SCRUBBER
1ST STAGE CYLINDER
ENGINE
2ND STAGE CYLINDER
1ST STAGE ACCUMULATOR
LC
LC
HYDROCARBON
2
WATER
GAS OUT
2ND STAGE ACCUMULATOR
LC
LC
HYDROCARBON
3
WATER

Figure 29. Two-stage gas compressor.

achieved in a compressor plant if refrigeration is used in place of cooling water in the compressed gas coolers.

6. LPG and Natural Gasoline Recovery by Oil Absorption

The absorption process for recovery of LPG and natural gasoline is more complex and generally more expensive than the compression and refrigeration process, but it is also more efficient. An absorption oil, usually in the kerosene range, is used to absorb the heavy hydrocarbon vapor under pressure. The hydrocarbon product is recovered from the absorption oil by distillation.

Figure 30 is a flow diagram for a typical oil absorption process. Gas is fed to the bottom of the main absorber where it is brought into countercurrent contact at relatively high pressure with cold lean absorption oil. Treated gas leaves the system from the top of the main absorber and rich absorption oil flows from the bottom to a flash tank. Enough product vapor is flashed along with the dissolved natural gas to warrant the use of a reabsorber column. Flashed gas and gas from the still are combined and fed to the reabsorber where they are brought into contact with a slip stream of lean absorption oil at low pressure. Overhead gas from the reabsorber goes to fuel. Rich oil from the reabsorber and the flash tank are combined and heated by exchange with still bottoms. The combined stream is heated by exchange with steam or hot gas oil and is sent to the still for regeneration by distillation. A small amount of steam is injected directly into the still to help strip the lean absorption oil. Most of the resulting

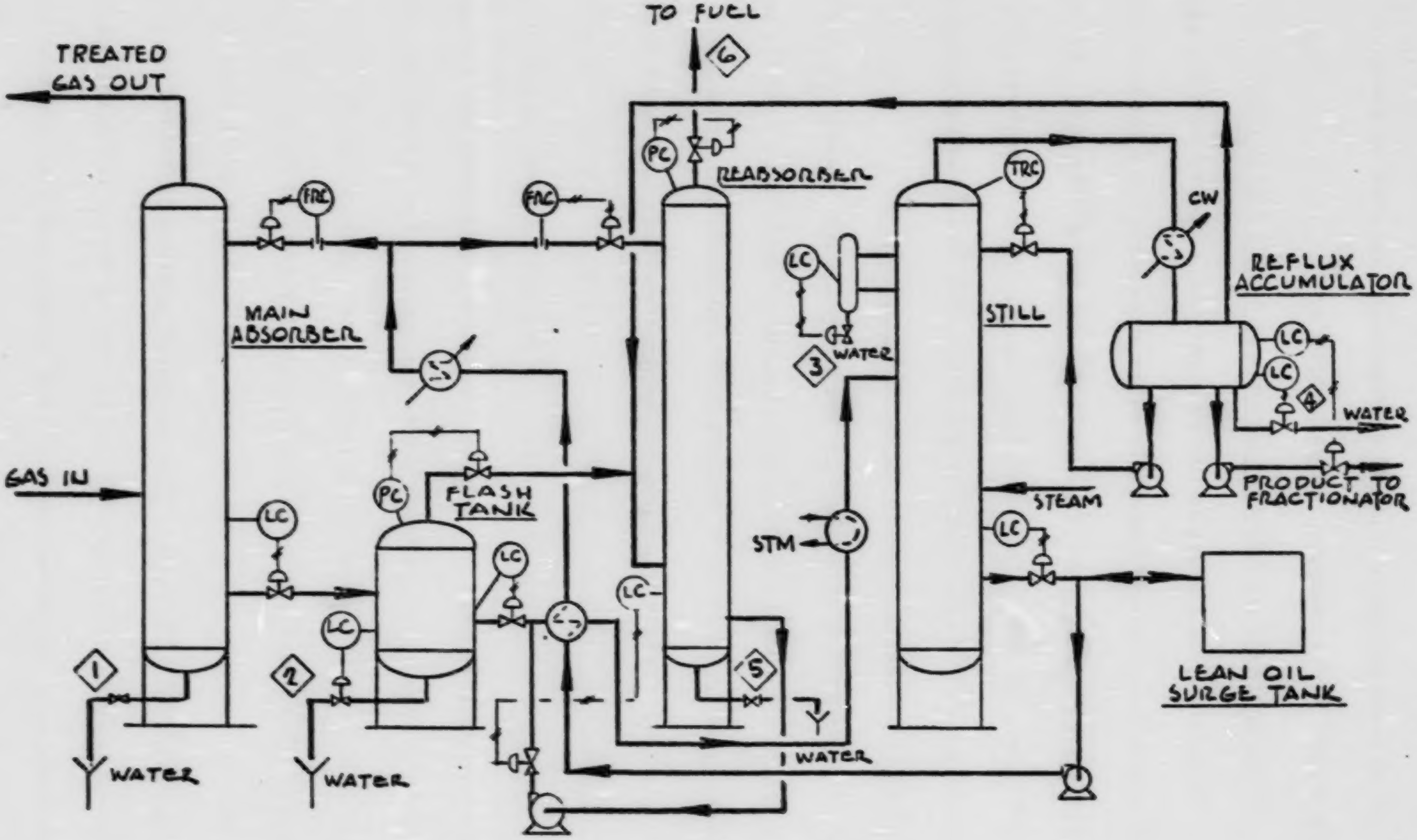

TREATED GAS OUT
GAS IN
MAIN ABSORBER
FRC
FRC
LC
1
WATER
2
WATER
LC
PC
LC
FLASH TANK
LC
TO FUEL
6
PC
REABSORBER
LC
3
WATER
STM
5
I WATER
STILL
TRC
STEAM
LC
CW
REFLUX ACCUMULATOR
LC
LC
4
WATER
PRODUCT TO FRACTIONATOR
LEAN OIL SURGE TANK

Figure 30. Oil absorption plant.

condensate is removed from the top trays of the still by the use of a draw off tray. Product hydrocarbon from the reflux accumulator is sent to a fractionator for distillation into LPG and natural gasoline. Hot lean absorption oil from the bottom of the still is cooled by feed-bottoms exchange and by cooling water exchange and is recycled to the absorbers.

Water entering the process in the feed gas and stripping steam is condensed in the system and leaves in streams (points 1-5 in the figure). These streams may contain sulfides. If so, they should be routed to a sour water stripper. Gas from the reabsorber (point 6) may contain hydrogen sulfide and may therefore require treatment before using as fuel.

Some absorption plants are operated at high pressure, on the order of 1,000 psig. In such cases, it may be desirable to employ two stills for absorption oil stripping. One still is operated at high pressure and one at low pressure. The advantage of this procedure is that better recoveries of product and cleaner separations are possible.

S. LIGHT ENDS RECOVERY

Refinery light ends are usually hydrocarbon compounds having four or less carbon atoms, including methane, ethane, propane, butane, and isobutane. The objective of a light ends recovery unit is to separate these components into saleable products and fuel gas. In small refineries, or in refineries where little or no cracking processes take place, light end recovery units may not be economical and most of the light ends are used as fuel. Larger refineries, on the other hand, may have more than one light ends recovery system, perhaps located in different sections of the refinery.

Normally, the ethane and methane go into the fuel gas system. Propane is separated as a product because of its value as a feed stock in the petrochemical industry. The butanes are either added to the gasoline pool, or separated to isobutane and normal butane and used as feed for other units in the refinery (see Section G, Alkylation Process). The process configuration and recovery of light ends will vary with the particular needs of the refinery. A typical unit is presented in Figure 31.

The feed to the recovery unit is unstabilized naphtha (a gasoline cut containing dissolved light ends) and a gas stream rich with propane and butanes. The naphtha feed is stabilized in the stabilizer by removing a portion of the light ends. Some butanes are left in the stabilizer bottoms product for maintaining the proper naphtha vapor pressure. The stabilizer overhead product is combined with other refinery gases and fed to a deethanizer. Methane and ethane are removed as fuel gas from the deethanizer accumulator and the deethanizer bottom product, essentially propane and butanes, is fed to the depropanizer for separation into the two products.

Pollution Sources

Possible point sources of pollutant emission are sour water from the deethanizer accumulator (points 1 and 2 in the figure). This

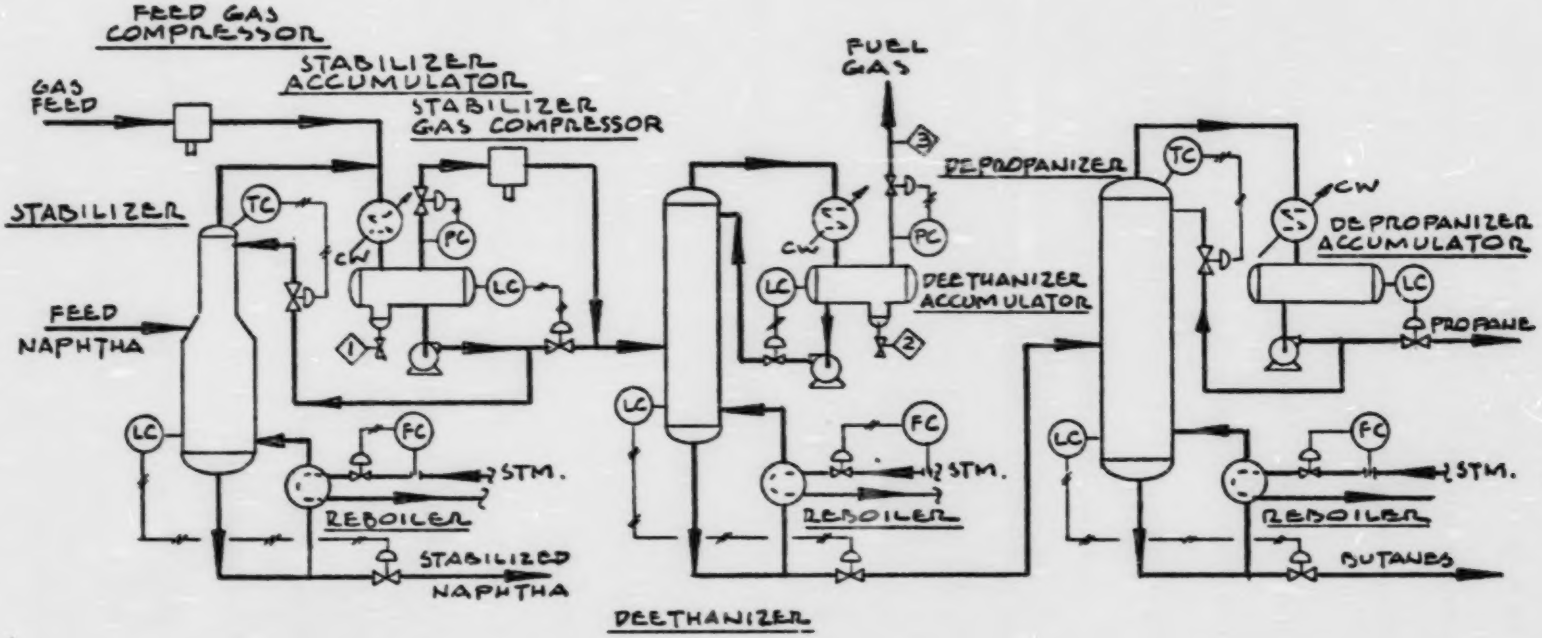

FEED GAS COMPRESSOR
STABILIZER ACCUMULATOR
STABILIZER GAS COMPRESSOR
GAS FEED
STABILIZER
TC
CW
PC
LC
FEED NAPHTHA
1
LC
FC
STM.
REBOILER
STABILIZED NAPHTHA
FUEL GAS
3
DEPROPANIZER
CW
PC
LC
DEETHANIZER ACCUMULATOR
2
LC
FC
STM.
REBOILER
DEETHANIZER
TC
CW
DEPROPANIZER ACCUMULATOR
LC
PROPANE
LC
FC
STM.
REBOILER
BUTANES

Figure 31. Light ends recovery.

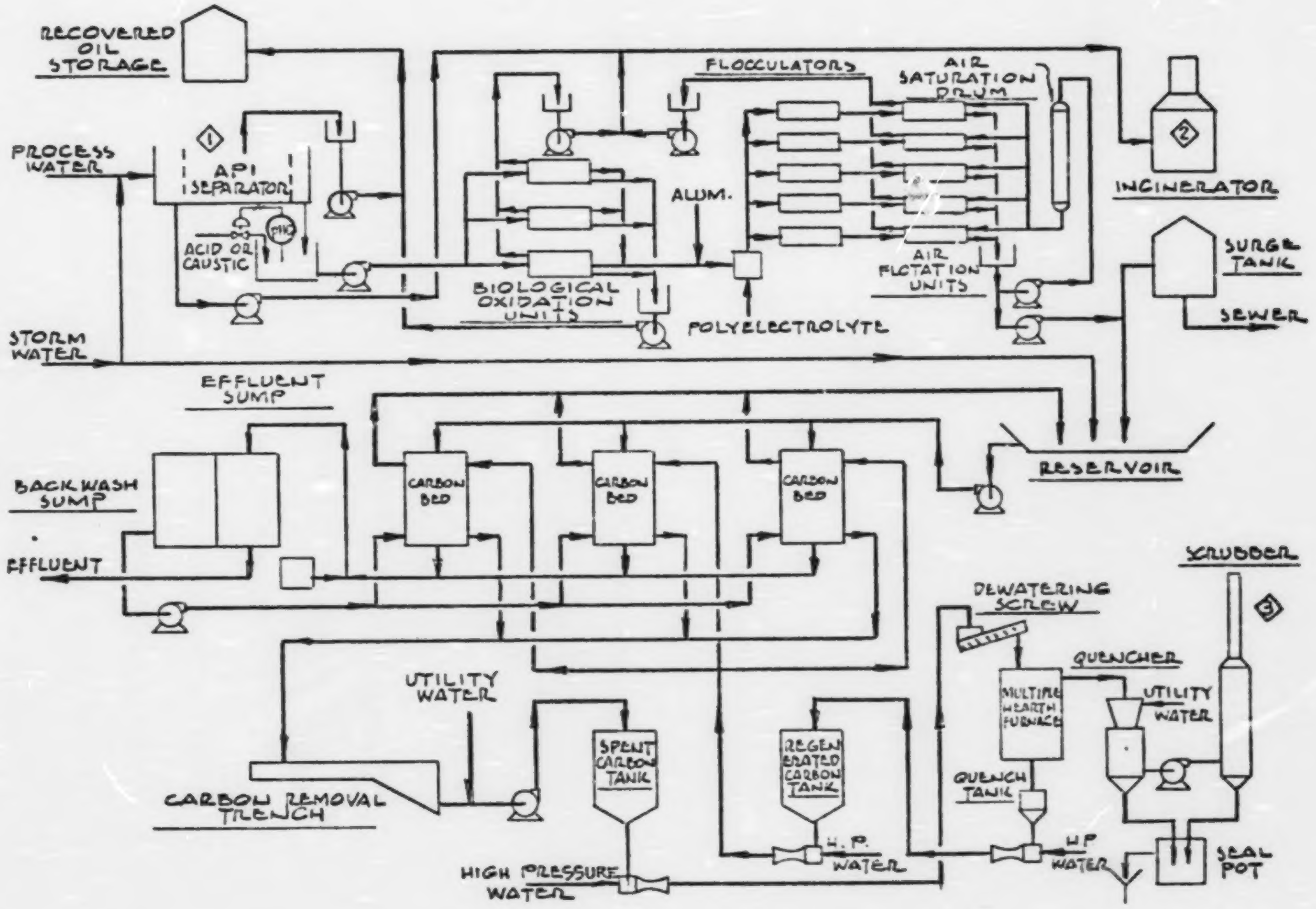
stream should be sent to a sour water stripper. Fuel gas (point 3) from the unit may contain H_2S, in which case it should be treated for H_2S removal before being used as fuel.

T. WASTEWATER SYSTEMS AND SOLIDS DISPOSAL

Refineries generate a significant amount of process water, which has been in contact with oil and chemicals. This wastewater stream requires extensive treatment before discharge into a body of water. In addition, large quantities of runoff from refinery process and storage areas during rainy periods require treatment before discharge. Figure 32 shows a relatively complex system for handling these water streams. The unit operations involved vary from refinery to refinery depending on local requirements. All refineries can be expected to have an API separator. Dissolved air flocculators are common, many units having been installed in the past few years. Biological oxidation units are less common, and there are only one or two carbon units in service. For more detail refer to Air Pollution Engineering Manual.

During dry weather operation, the process water streams are collected and flow to an API separator. The oil skimmings are pumped to a storage tank to await treatment. The sludge that settles in the separator may be either pumped to an incinerator or removed by tank truck for disposal. The pH of the water leaving the separator is controlled at 7.0 to 7.5 by the addition of either acid or caustic.

This water is frequently pumped to a biological oxidation system


RECOVERED OIL STORAGE
PROCESS WATER
①
API SEPARATOR
ACID OR CAUSTIC
PHC
STORM WATER
BIOLOGICAL OXIDATION UNITS
ALUM.
POLYELECTROLYTE
FLOCCULATORS
AIR SATURATION DRUM
AIR FLOTATION UNITS
②
INCINERATOR
SURGE TANK
SEWER
EFFLUENT SUMP
BACK WASH SUMP
EFFLUENT
CARBON BED
CARBON BED
CARBON BED
RESERVOIR
UTILITY WATER
CARBON REMOVAL TRENCH
SPENT CARBON TANK
HIGH PRESSURE WATER
REGENERATED CARBON TANK
H. P. WATER
DEWATERING SCREW
MULTIPLE HEARTH FURNACE
QUENCH TANK
H.P. WATER
QUENCHER
UTILITY WATER
SCRUBBER
③
SEAL POT

32. Waste water system and solids disposal.

to reduce the biological oxygen demand (BOD). Further removal of suspended solids and oil from the water is effected by chemical flocculation, using a combination of alum and a polyelectrolyte flocculent, followed by air flotation. Sludge from biological oxidation and the skimmings from air flotation may be either pumped to an incinerator or removed by tank truck for disposal. The water has now been treated sufficiently to be pumped to a surge tank and then to a municipal sewer if one is available.

Further treatment may be required before the water can be discharged to a natural water body. The wastewater is collected in a reservoir, and the final or tertiary treatment for the removal of dissolved organics is effected by passage through activated granulated carbon beds. The water is then chlorinated and flows to a retention sump before being discharged from the plant.

The carbon beds are reactivated by backwashing with treated water. Removed contaminants flow back to the wastewater reservoir. When the carbon is spent, it is removed from the beds in slurry form and placed in storage tanks. The carbon is regenerated by educting from the tank to a dewatering screw and feeding to a multiple hearth furnace. Contaminants are burned off as the carbon drops through the furnace. The carbon falls into a quench tank and is educted to a storage tank ready for reuse. Flue gases from the furnace are quenched and then scrubbed before venting.

During periods of rain, the process waters, mixed with rain water, continue to be processed through the normal treating facilities. The maximum rate through this system is limited by the capacity of the biological oxidation and air flotation units. Water runoff in excess of the capacity of the system is pumped to the reservoir. Oil skimming facilities should be provided in the reservoir for surface oil removal. This water can then be pumped and processed through the activated carbon adsorption plant before being discharged from the plant.

Pollution Sources

Tanks that are open to the atmosphere are potential sources of pollutants, thus the API separator (point 1) should be designed with a cover where required to comply with pollution control standards for oil-effluent water separation equipment.

Another source (point 2) is the stack gas from the incinerator. This equipment should also be designed to comply with local pollution control standards.

A third potential source of emission (point 3) is the vent gas from the carbon regeneration system.

U. FLARE AND BLOWDOWN SYSTEM

During refinery processing plant upsets and plant emergency conditions, such as power failures, higher than normal pressure may be generated in certain equipment. To protect this equipment from damage, pressure relief devices are installed and set to open at a pressure below the design pressure of the equipment. Process materials released when these valves open are collected and burned by a flare (see Figure 33). Process waste gas is sometimes also flared.

Under normal operating conditions, when no systems are relieving to the flare header, a small purge of fuel gas is used to keep a positive pressure in the line and the flare flame alight. During emergency conditions the relieved process fluids flow through the flare header to the knock out drum, where any entrained liquid is separated. The vapors from this drum flow through a liquid seal to the flare and are burned. The liquid is pumped to a slop tank.

Pollution Sources

The only potential source of air pollution from this system is the stream containing the products of combustion of the flare (point 1 on the figure). Any of the refinery processing plants could relieve to the flare, including those containing H_2S and other pollutants; but air pollution regulations do not usually cover emergency situations. A continuing emission problem could occur if relief valves do not reseat properly, leaking process fluids to the flare system. Preventing such leakage is a matter of proper maintenance. Additional information on flares is presented in Chapter II.

V. STORAGE

Normal refinery operation requires the storage of large volumes of crude oil, intermediates, and finished products. Many of

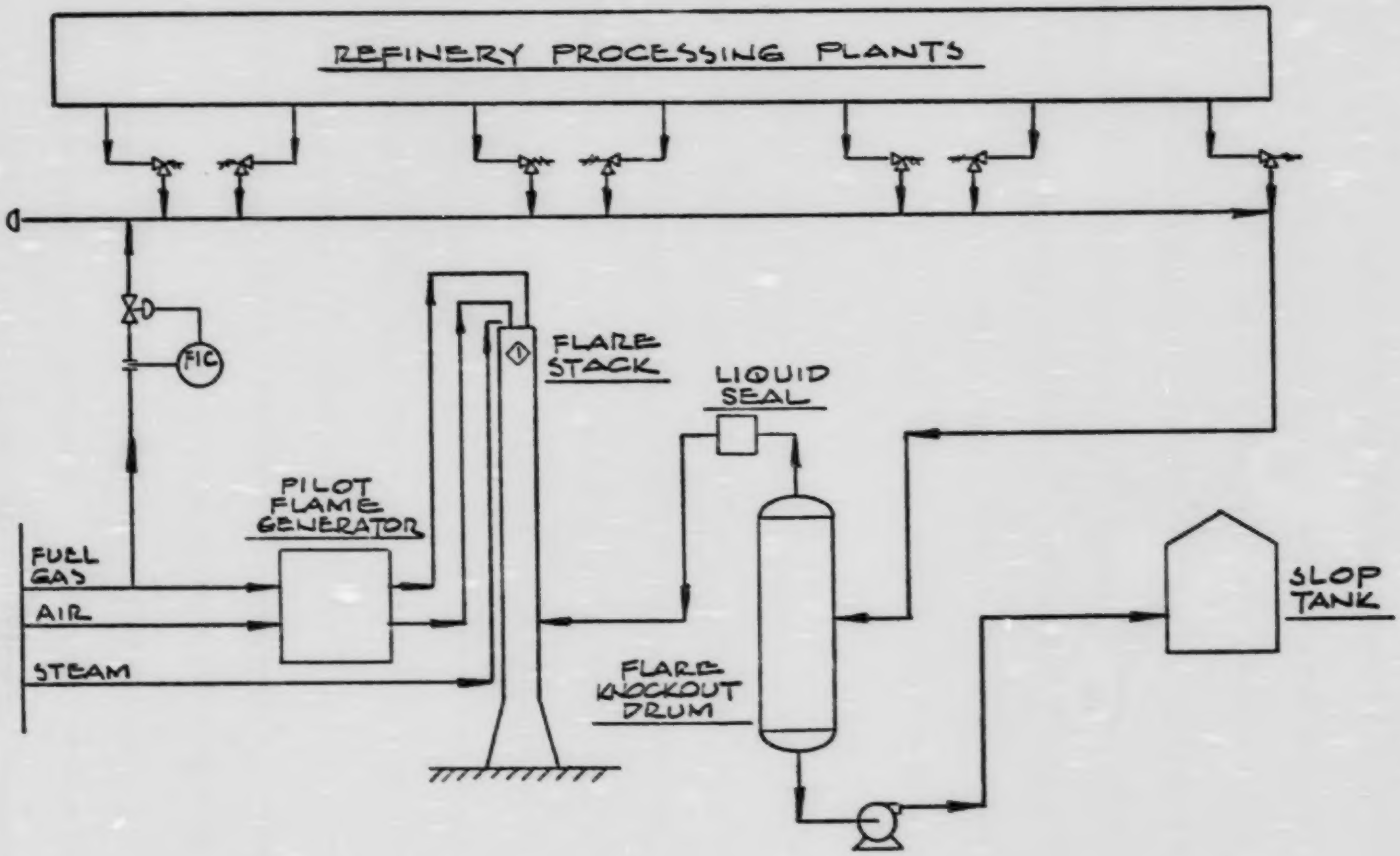

REFINERY PROCESSING PLANTS
FIC
FLARE STACK
LIQUID SEAL
PILOT FLAME GENERATOR
FUEL GAS
AIR
STEAM
FLARE KNOCKOUT DRUM
SLOP TANK

Figure 33. Flare and blowdown system.

these materials are volatile and, unless properly controlled, storage can be a major source of hydrocarbon pollutants.

Hydrocarbon emissions from volatile fuel storage can be controlled by not allowing space for vapor formation, confining the vapors within the storage system, collecting and burning the vapors, and by collecting the vapors and recovering the hydrocarbon portion. Although adequate control can be achieved for any storage facility by any of these methods, the best method to use depends on the characteristics of the storage facility and fuel to be stored.

1. Floating Roof Tanks

The principle used in floating roof tanks is the elimination of vapor spaces. This is accomplished by floating a rigid deck or roof on the surface of the stored liquid. The roof then rises and falls according to the depth of stored liquid. The roof is equipped with a sliding seal at the tank wall so that the liquid is completely covered. No additional roof is required; however, many tanks are equipped with a standard fixed roof that covers the floating roof. Floating roof tanks are suitable for volatile fuel storage where the fuel is stored below its boiling point. That is, the vapor pressure of the fuel must be below atmospheric pressure at storage conditions.

Sliding seals are an important feature of all floating roofs. The ideal seal will be vapor tight, long lasting, and require little maintenance. Seals are required at the rim of the roof, at support columns, and at all points where tank appurtenances pass through the roof. Two basic types of seals are in common use today, the metallic and the nonmetallic seal. The metallic seal consists of a sheet metal shoe held against the tank wall by springs or counter weights. The space between the roof and the shoe is covered by a flexible fabric membrane. The fabric is often protected by a metal cover.

The nonmetallic seal is usually made of a hollow flexible plastic tube filled with plastic foam, liquid, or compressed air. Column and guide cable seals are usually close-fitting, flexible plastic sheets. The sheets cover holes cut in the floating roof and are sealed at the edges of the holes by resting on plastic or metal rims fitted around the holes. The sheet is sometimes allowed to slide horizontally on the rim to provide for vertical misalignment of the column.

Floating roofs are taken as the standard of effective emission control for storage tanks. Their effectiveness depends on the material stored and other factors, but their use results in about a 90% reduction of emissions.

2. Variable Vapor Space Tanks

There are two general types of variable vapor space, or conservation, tanks that have been used in volatile fuel storage systems. Lifter roof tanks have a movable roof that rises or falls as the volume of vapor changes. Flexible diaphragm tanks have a diaphragm installed within the tank and attached to the wall so as to provide a variable vapor space in the lower half of the tank, with the diaphragm protected by the upper half of the tank.

It would be possible to provide enough vapor space within a system to prevent the escape of vapor during both loading and normal breathing, but the volume required would be almost equal to the liquid storage volume. Such a system would be too expensive to be practical. In the past, lifter roof tanks have been used to prevent tank breathing losses. No attempt to prevent loading losses was made, the excess volume being vented to the atmosphere. Since the degree of control provided by such systems will not meet current pollution control requirements, the use of variable vapor space tanks as primary control devices has been discontinued. They are, however, still used to provide surge volume in systems employing absorber units and the like. (See Section W, Loading and Transfer.)

3. Flares and Incinerators

Hydrocarbon emissions from storage systems can be controlled by piping the vapors to a flare or incinerator for burning. Since the hydrocarbons are destroyed in the process, this procedure results in an economic loss. The procedure is sometimes justified for isolated tankage, but most refineries employ floating roof tanks and/or vapor recovery systems.

4. Vapor Recovery Systems

Occasionally vapor recovery systems of the type described in Section W, Loading and Transfer, are used for control of storage systems (or tank farms). A more generally used system, however, is one in which the storage tanks are blanketed with natural gas. (That is, the tanks are manifolded together and a slight positive pressure of natural gas is maintained in the manifold.) When vapor is generated in this system, the excess is compressed and sent to the refinery fuel system. In larger systems, where the cost of the additional equipment is justified, light ends recovery may be employed (see Section S).

Figure 34 is a schematic diagram for a typical refinery storage vapor recovery system. Standard cone roof tanks are interconnected with a piping manifold. Since the tanks can withstand a pressure or vacuum of only a few inches of water in the vapor space, the tanks are equipped with combination pressure-vacuum relief valves. The system should be designed so that these valves remain closed. The proper pressure is maintained by admitting natural gas to the manifold when the pressure falls, and by removing vapor by means of the compressor when pressure rises. Normally, the compressor is run continuously so as to maintain a vacuum in the surge tank at the compressor inlet. The fuel gas stream may contain sulfur compounds (point 1 in figure).

5. Estimated Hydrocarbon Losses

Annual fuel losses can be estimated by a method given in a manual prepared by the American Petroleum Institute, API Publication No. 4080, Recommended Procedures for Estimating Evaporation and Handling Losses of Volatile Petroleum Products in Marketing Operations, July 1971. The appropriate nomographs from this publication are

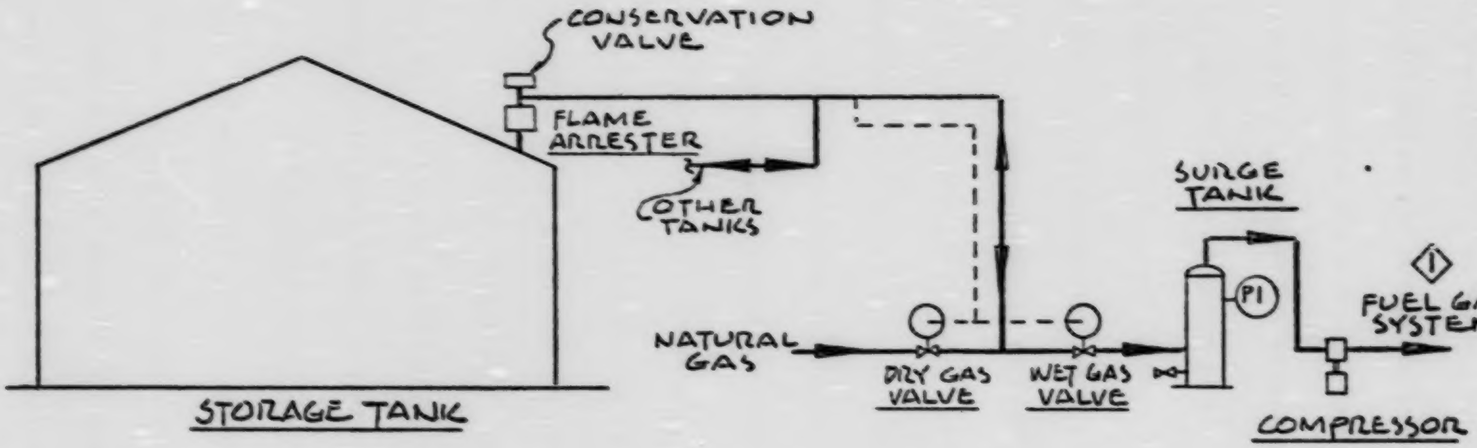

CONSERVATION VALVE
FLAME ARRESTER
OTHER TANKS
SURGE TANK
PI
1
FUEL GAS SYSTEM
NATURAL GAS
DRY GAS VALVE
WET GAS VALVE
STORAGE TANK
COMPRESSOR

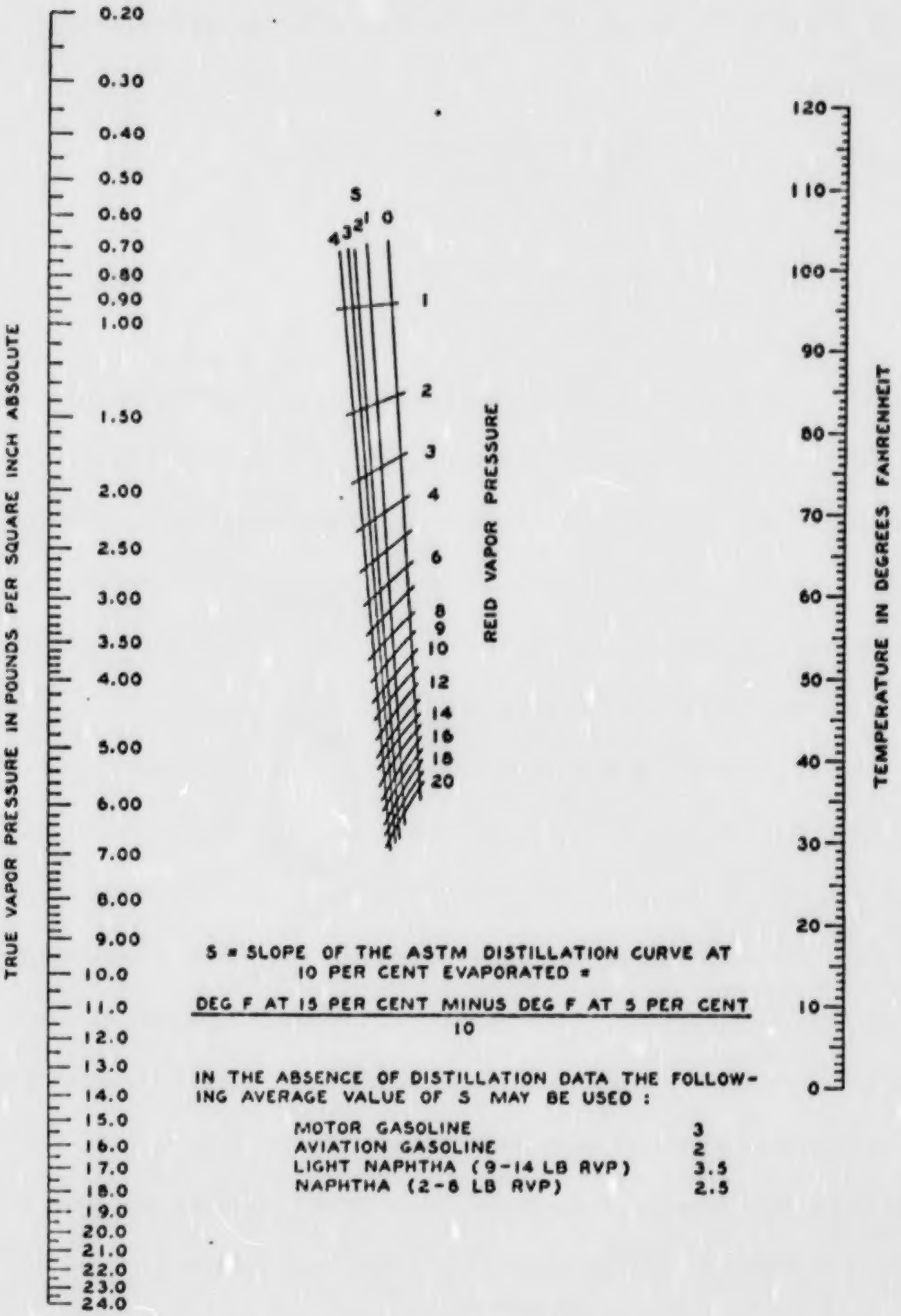
Figure 34. Vapor recovery for storage.

shown in Figures 35, 36 and 37. The factors affecting hydrocarbon loss include:

- Daily temperature change
- Fuel volatility
- Loading frequency
- Paint
- Storage temperature
- Tank diameter
- Tank outage

Fuel volatility is normally expressed in terms of vapor pressure. Reid Vapor Pressure is commonly used. It is the vapor pressure at 100°F as determined by a test method that employs a specified apparatus. Because of the apparatus used, Reid Vapor Pressure is not a true vapor pressure. If the true vapor pressure is required, it is usually found by using an experimentally developed correlation.

Vapor pressure is a measure of the pressure developed by a liquid, at a given temperature, in the vapor space over the liquid. It applies to a closed container containing only the liquid and vapor from the liquid. The vapor pressure depends only on the composition of the liquid and on the temperature. If the vapor pressure is equal to atmospheric pressure, the liquid is at its boiling point. Materials such as gasoline are normally stored at temperatures below their boiling points. The vapor space of the tanks, therefore, contains mixtures of hydrocarbon and air. For practical purposes, the volume percent of hydrocarbon in the mixture at equilibrium is equal to the ratio of liquid vapor pressure to total system pressure, expressed as percent. The



S = SLOPE OF THE ASTM DISTILLATION CURVE AT 10 PER CENT EVAPORATED =

$$\frac{\text{DEG F AT 15 PER CENT MINUS DEG F AT 5 PER CENT}}{10}$$

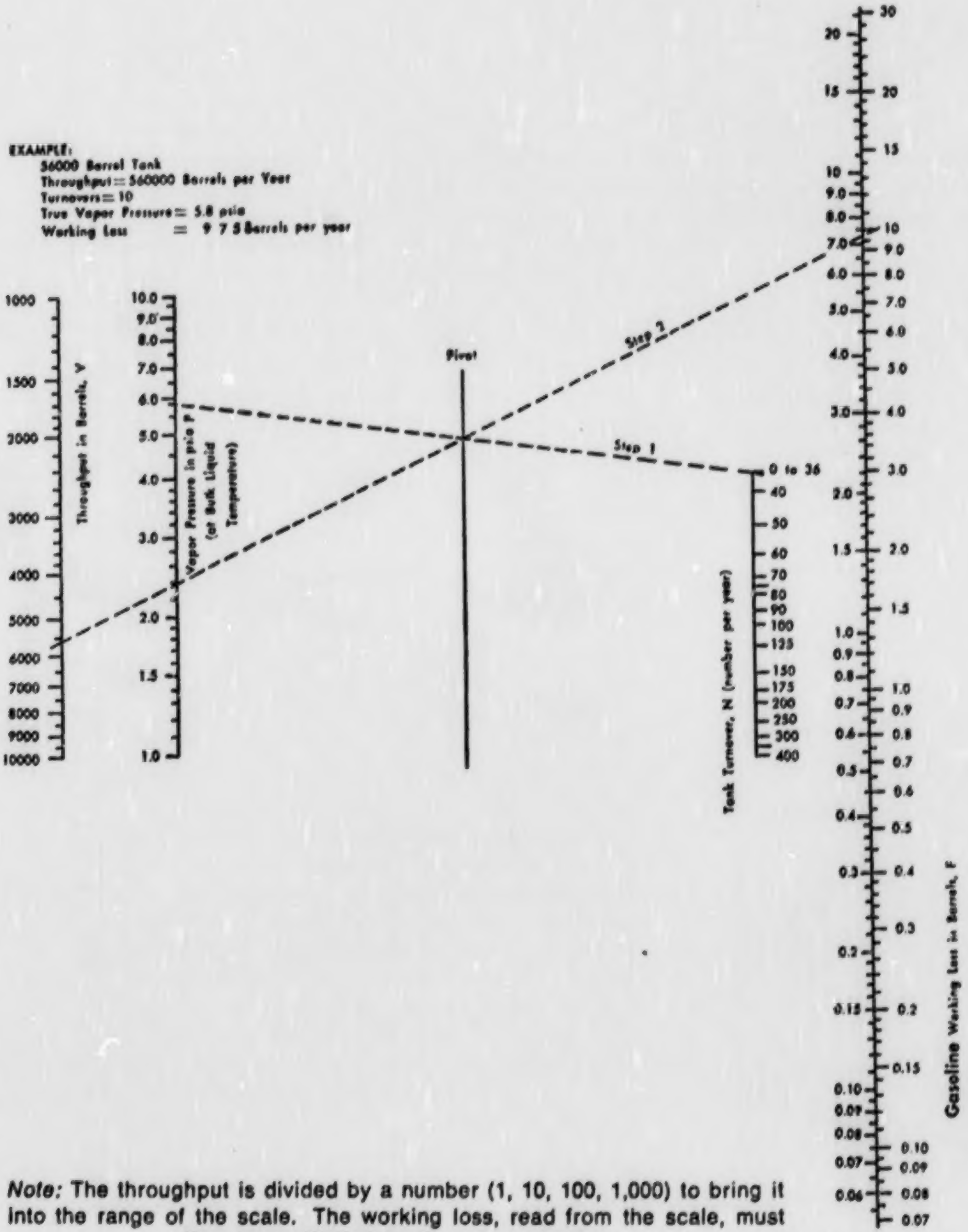
IN THE ABSENCE OF DISTILLATION DATA THE FOLLOWING AVERAGE VALUE OF S MAY BE USED :

MOTOR GASOLINE	3
AVIATION GASOLINE	2
LIGHT NAPHTHA (9-14 LB RVP)	3.5
NAPHTHA (2-8 LB RVP)	2.5

Source: Nomograph drawn from data of the National Bureau of Standards.

(API PUBL. NO. 4080)

Figure 35. Vapor pressures of gasolines and finished petroleum products.



Note: The throughput is divided by a number (1, 10, 100, 1,000) to bring it into the range of the scale. The working loss, read from the scale, must then be multiplied by the same number.

(API PUBL. NO. 4060)

Figure 36. Working loss of gasoline from fixed-roof tanks.

(API PUBL. NO. 4080)

EXAMPLE:
T = 16°F
F_p = 1.33
H = 23 Feet
P = 5.8 psia
D = 100 Feet
L_y = 1350 barrels per year

Tank Color		Paint Factor, F_p	
Roof	Shell	Paint in Good Condition	Paint in Poor Condition
white	white	1.00	1.15
aluminum (specular)	white	1.04	1.18
white	aluminum (specular)	1.16	1.24
aluminum (specular)	aluminum (specular)	1.20	1.29
white	aluminum (diffuse)	1.30	1.38
aluminum (diffuse)	aluminum (diffuse)	1.39	1.46
white	gray	1.30	1.38
light gray	light gray	1.33	1.46
medium gray	medium gray	1.46	1.46

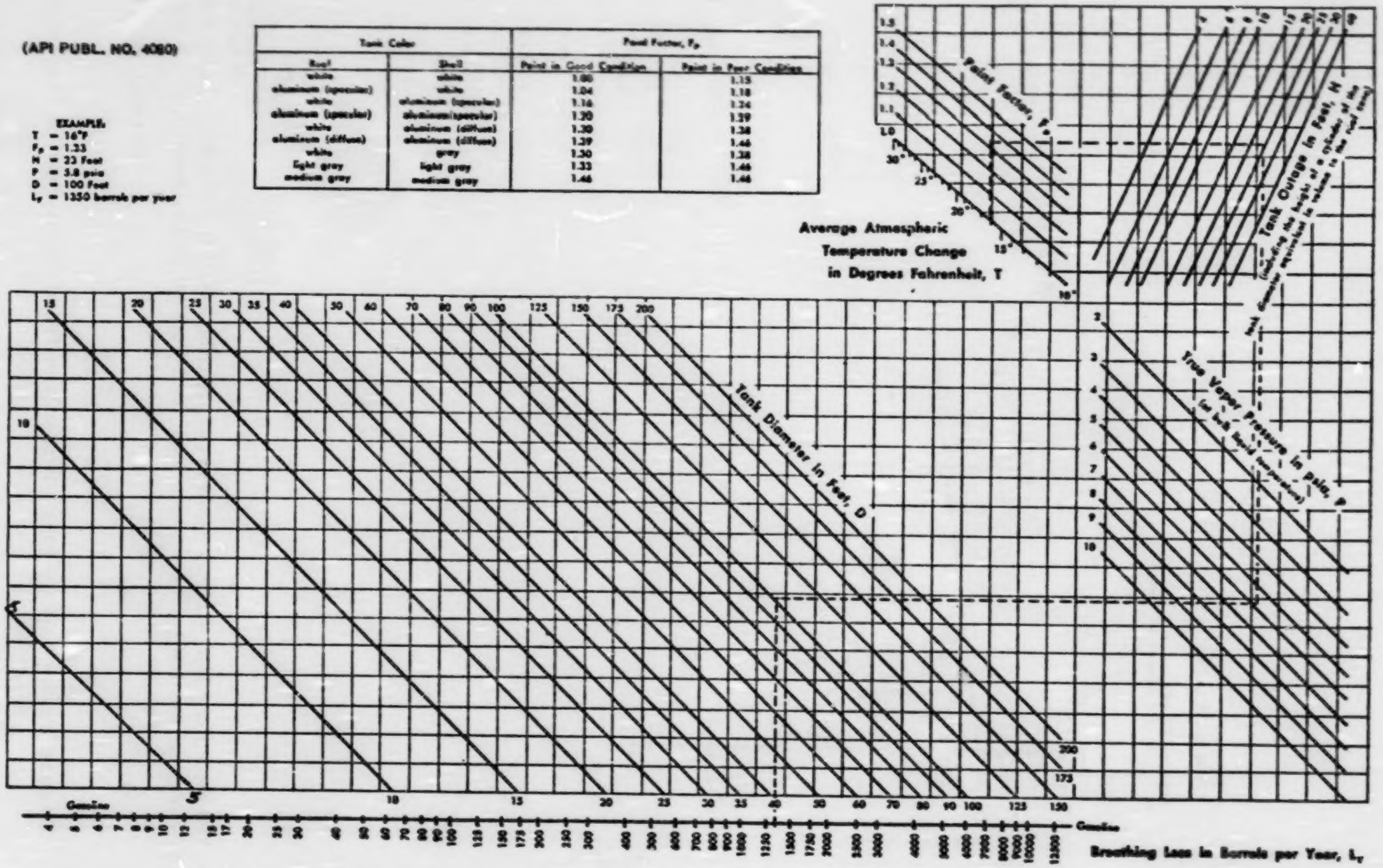


Figure 37. Breathing loss of gasoline from fixed-roof tanks.

amount of hydrocarbon lost in a given volume of vapor displaced from a tank is thus a direct function of the vapor pressure of the stored liquid.

Loading frequency is a measure of the number of times a tank is filled and emptied in a given period of time. It is usually expressed as "turnovers per year". When liquid is loaded into a tank, an essentially equal volume of vapor is displaced. The amount of hydrocarbon lost is a function of other factors as well but is strongly dependent on the total volume of vapor displaced and, therefore, on the turnovers per year.

The temperature at which a given fuel is stored determines the vapor pressure and hence the equilibrium vapor composition. The higher the temperature, the higher the hydrocarbon content of the vapor and the greater the loss per volume of vapor. In vapor loss correlations, the Reid Vapor Pressure and the storage temperature are used to specify vapor composition, and the composition itself may not ever be determined explicitly.

Daily temperature change causes a cyclical change in the temperature of the stored liquid and of the vapor space above the liquid. Increasing liquid temperature results in increasing liquid vapor pressure, and some of the liquid is vaporized. At constant pressure, not only is the percent of hydrocarbon in the vapor increased, but vapor is displaced from the tank. Another effect of increasing temperature is that the vapor in the vapor space expands. Unless the tank pressure is increased, vapor is displaced from the tank. When temperature drops, the reverse occurs and air is drawn into the tank vapor space.

Breathing losses are a function of vapor space volume (or tank outage); the greater the volume, the greater the loss. Losses from tanks that are nearly empty will be greater than losses from tanks that are full. For a tank of a given diameter, the vapor volume can be specified by stating the height from the top of the tank to the liquid surface. This height is called outage. When calculating breathing losses, it is common practice to assume that the tanks are half full; that is, outage is taken as equal to one-half of the total tank height.

If the liquid and vapor in a tank were always in equilibrium, tank diameter would only be a means of stating volume. In actual field testing, however, it has been found that the tank vapors are not always saturated and that vapor losses are somewhat less than would be otherwise expected. Smaller tanks were found to have lower losses, but the difference is not significant for tank diameters of 30 feet or more.

The color and condition of the paint on a tank have been found to have an important effect on breathing losses. Using white paint in good condition as a standard, white paint in poor condition may lead to a 15% increase in loss. A medium grey paint may lead to a 46% increase.

All of these factors are included in the nomographs. The nomograph in Figure 35 can be used to obtain the true vapor pressure from the more commonly available Reid vapor pressure. That in Figure 36 can be used to estimate working loss, that is, the loss due to loading operations and the nomograph in Figure 37 can be used to estimate breathing loss, that is the loss due to daily temperature changes.

6. Potential Point Sources of Pollutants

Vents on uncontrolled cone roof tanks storing volatile hydrocarbons are a source of pollutants and should be controlled.

Sliding seals and gage-opening covers on floating roof tanks must be properly maintained or they will leak.

Conservation valves on tanks connected to a vapor recovery system may leak. The leakage may be due to a system pressure that is higher than the set pressure of the valve or to an improperly maintained valve seal.

W. LOADING AND TRANSFER

Gasoline and other petroleum products require distribution from the refinery to the consumer. This is achieved by pumping from refinery storage tanks to a loading terminal where the products are loaded into tank cars, barges, and tank trucks by means of loading racks. Products are also loaded into ocean-going tankers at bulk marine terminals by pumping from storage. Marine terminals may have facilities for unloading crude oil from tankers into storage tanks. During all these loading and transfer operations large amounts of air containing hydrocarbon vapors are generated. If not controlled, these vapors can be an important source of air pollution.

1. Loading Equipment

Loading racks are structures containing the platforms, piping, vapor collection devices, control devices, and loading arm assemblies required for transferring the product from storage to the transport vehicle. Bottom loading normally requires simpler equipment than overhead loading. The method used for loading marine tankers is similar to the bottom-loading operation. Liquid is delivered to the bottom of a compartment while vapors are vented through a manifold.

To avoid atmospheric pollution the produced vapors are collected at the tank vehicle hatch using specially designed closure devices. For overhead loading these are plug-shaped devices that have a central channel for the liquid to flow into the tank and an annular space for the vapor to flow out of the tank into a pipe connected to a vapor disposal system. For bottom loading a vapor take-off line is connected between the vapor space of the tank and a vapor disposal system.

2. Vapor Recovery Systems

a. Vapor Recovery to Fuel Gas - When a suitable fuel gas system is available, the vapors can be used for fuel. The loading system is gas blanketed to avoid explosive mixtures, and the vapors are collected in a vapor holder. The vapors are fed to a compressor and discharged to the fuel gas system.

b. Vapor Recovery by Absorption in Gasoline - Figure 38 presents a typical system for the absorption of hydrocarbons in

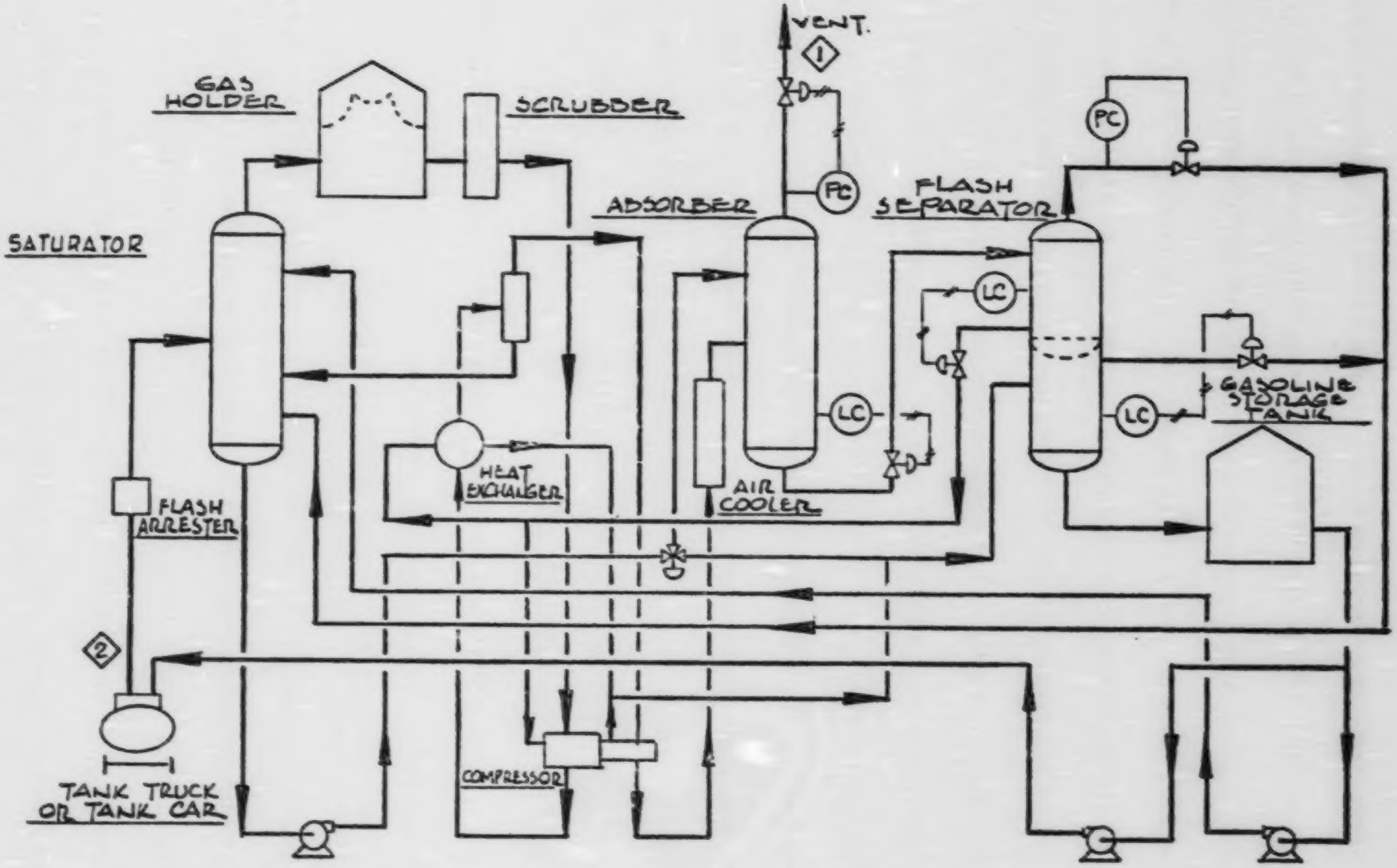

VENT.
1
GAS HOLDER
SCRUBBER
ABSORBER
PC
FLASH SEPARATOR
PC
SATURATOR
LC
LC
LC
GASOLINE STORAGE TANK
HEAT EXCHANGER
AIR COOLER
FLASH ARRESTER
2
TANK TRUCK OR TANK CAR
COMPRESSOR

Figure 38. Loading rack vapor recovery system.

gasoline. Explosive mixtures cannot be permitted in this unit so the amount of hydrocarbon in the air is raised substantially above combustible limits by saturating with gasoline. This is accomplished by countercurrent contact of the air with gasoline in the saturator prior to storage in the gas holder. The vapors are compressed, cooled and introduced into an absorption column where absorption of the hydrocarbon in gasoline takes place. The air is vented to the atmosphere through a back pressure control valve. The gasoline is returned to storage after the dissolved air is removed in the two-stage flash separator. Although the design recovery of hydrocarbon vapor by this system can be in excess of 90 percent, the vented air (point 1 in the figure) may be a potential source of pollution and may require checking. If the hatch closure (point 2) is not operating properly, air pollution may occur.

c. Vapor Disposal to Flare - The vapors can be satisfactorily disposed of by burning in a smokeless flare.

3. Loading Losses

Loading losses are influenced by many variables. The volume of vapors produced during loading is influenced by the mode of loading employed. The modes in general use in refinery operations are overhead loading and bottom loading. Overhead loading is subdivided into two types, splash filling and submerged filling. In splash filling, the outlet of the delivery tube is normally above the liquid level, while in submerged filling the outlet is below the liquid level. The former generates more hydrocarbon vapors.

To calculate loading losses, the total throughput information is recorded on a form such as that shown in Table 7. The true vapor pressure (TVP) is determined from the nomograph in Figure 35 for each product. The curves in Figure 39 can be used to calculate the evaporation as volume percent of load for splash loading and submerged loading in tank cars and tank trucks. The correlation curve in Figure 40 can be used to determine marine evaporation losses. A detailed discussion of these calculations can be found in API Publication No. 4080 (July 1971).

X. FUEL GAS SYSTEMS

Operators would like to maintain a fuel gas balance in their refineries to produce enough fuel gas to supply the heat required in the refining processes. However, production and use of fuel gas depend on the refinery processes, the crude processed, and economics. In general, additional fuel gas must be purchased. The crude unit and all of the cracking process units produce fuel gas. In most cases these gases contain sulfur compounds and have to be treated before entering the fuel gas system.

The fuel gas system is the storage and piping network by which the refinery stores, blends and distributes the gas internally in the refinery. The input to the fuel gas system is in general from two

Table 11. LOADING LOSSES: MOTOR GASOLINE, TURBINE FUELS, AVIATION GASOLINE

Plant____________________ Company____________________

Location: City____________________ State____________________ Year__________

Product	Total Thruput M Gallons	Total Deliveries M Gallons Tank Car or Tank Truck			Product Temp. °F	Vapor Pressure		Losses Bbls/Yr. (3)
		Marine	Splash (1)	Sub-Surface (2)		RVP PSI	TVP PSIA (3)	

(1) Splash Loading - free fall of product during loading. (2) Subsurface Loading - product delivered to bottom of compartment without splashing. Direct bottom delivery or top loading thru long spout achieves this effect. (3) To be calculated.

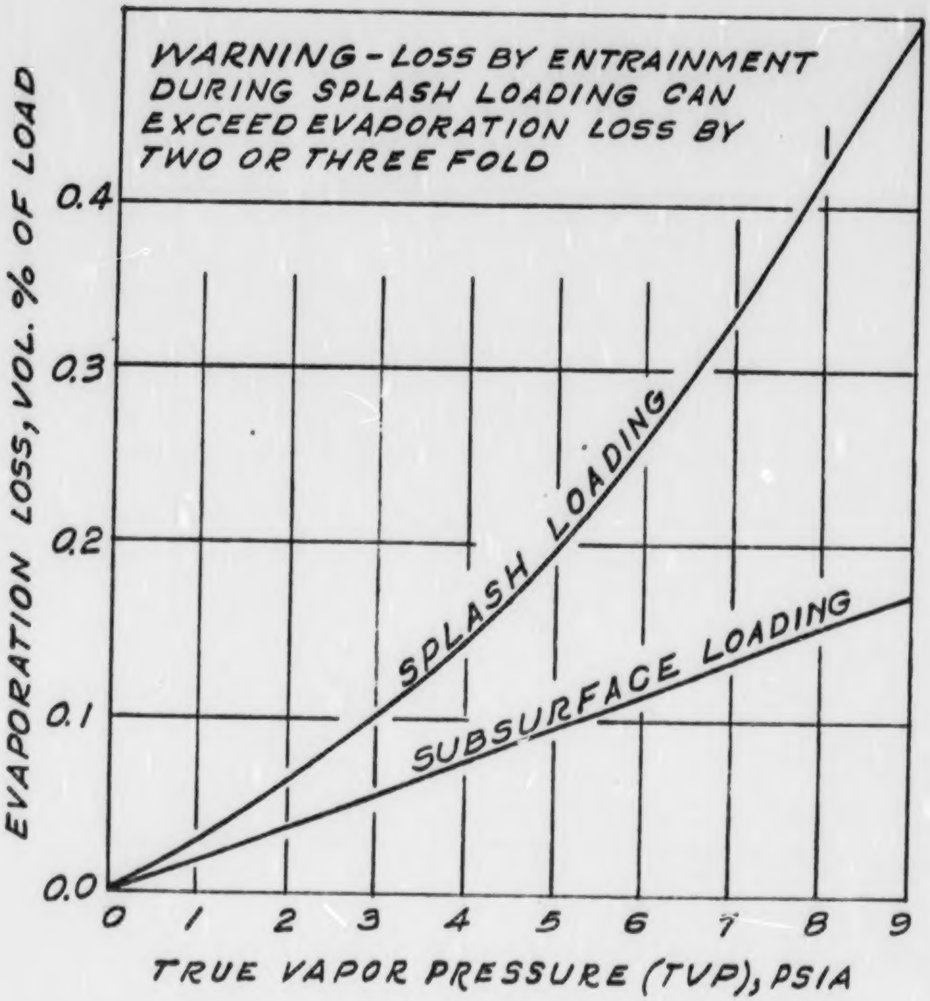


Figure 39. Loading losses for tank trucks.

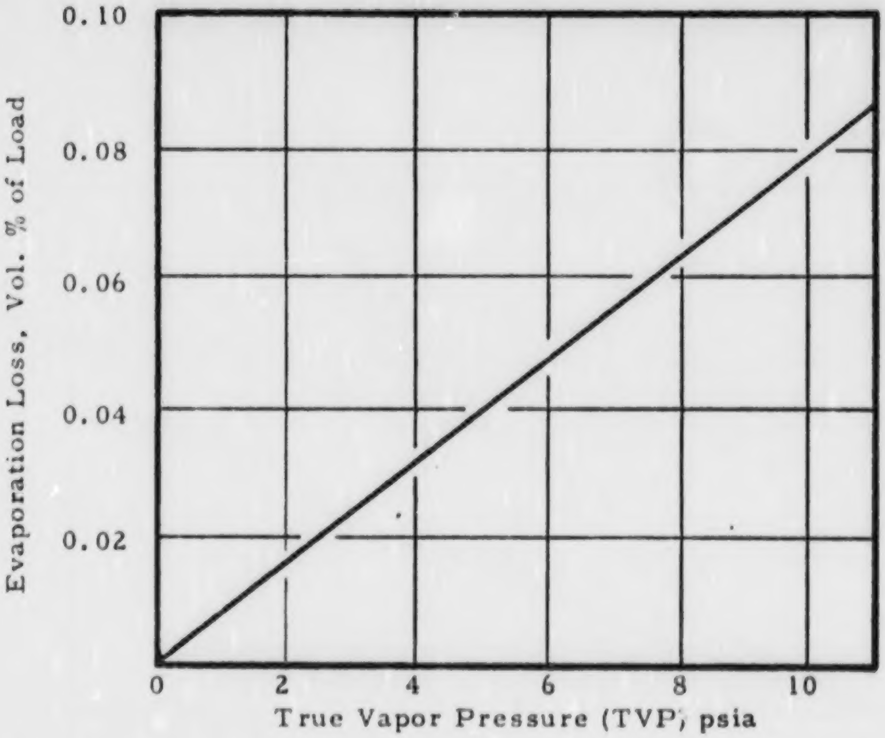


Figure 40. Loss from loading tankers and barges.

sources; from the treating unit where the sour gases produced in the refinery are treated for the removal of sulfur and from the gas purchased outside.

A diagram of such a system is presented in Figure 41. A knockout drum is provided to collect any liquid that may condense from the gas stream and to provide minimal storage for averaging high and low demands by the refinery. The fuel gas produced by the refinery flows into the system on a back-pressure control from the higher pressure level in the treating unit. When the demand exceeds the supply of gas produced within the refinery, the pressure in the knockout drum declines and purchased gas is allowed into the system. When the supply of refinery gas exceeds the demand of the refinery, the excess gas is flared. The system in general is well contained, with minimum emission sources. However, fuel gas produced in the refinery should be checked to see that it is free of sulfur compounds (point 1 in the figure) and any excess gas should be flared (point 2).

Y. STEAM GENERATION

Steam is used as a heating medium in various refinery operations and as a process fluid in others suchas hydrogen production and steam stripping.

Plant steam systems are normally closed cycles in which the steam generated yields its heat to process streams in heat exchangers by condensation. The condensate is returned to the steam generators

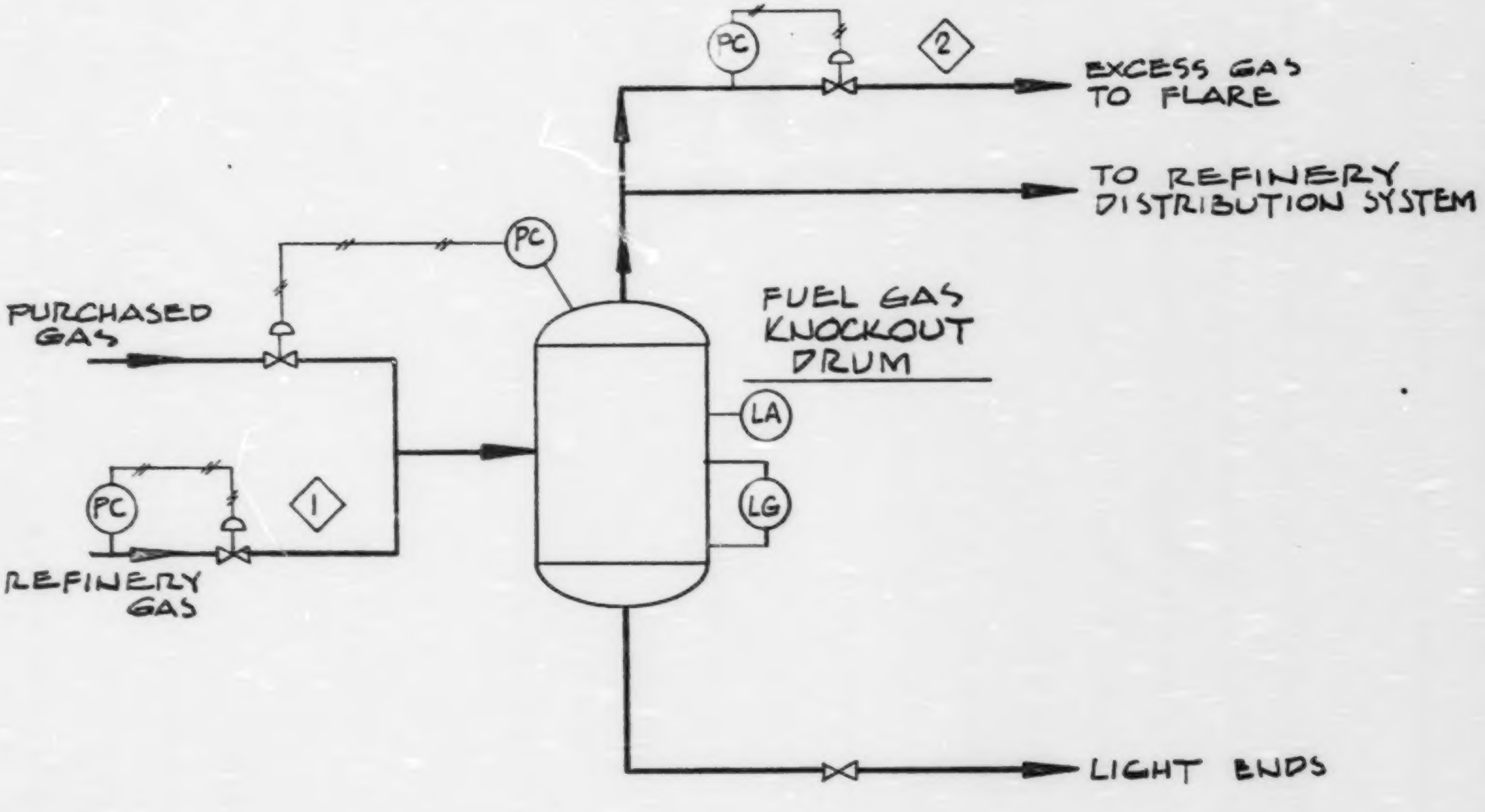

PURCHASED GAS
REFINERY GAS
PC
PC
PC
1
2
FUEL GAS KNOCKOUT DRUM
LA
LG
EXCESS GAS TO FLARE
TO REFINERY DISTRIBUTION SYSTEM
LIGHT ENDS

Figure 41. Refinery fuel gas system.

to be vaporized again. A relatively small make-up water stream is required to replace losses and blowdown from the system. The process flow sheet is shown on Figure 42.

Utility water is normally used as make-up water to the system. This water is treated by either softening or deionization. Air dissolved in the treated water is removed by steam stripping in the deaerator after which it is mixed with the recycle condensate. The water is pumped from the deaerator to the steam drum for conversion into steam.

The boiler may be fired by either fuel gas, fuel oil, or coal. Whichever fuel is used, the stack gases may be a source of atmospheric pollutants (point 1 in the figure). The deaerator vent could emit pollutants to the atmosphere if there is leakage of hydrocarbons from the process side into the steam side of a heat exchanger. This stream (point 2) should be checked regularly for hydrocarbon contamination.

Z. COOLING TOWER

Water is used as the medium for removing heat from various refinery streams. Plant cooling water systems are normally closed cycle (see Figure 43). Water from the cooling tower picks up heat from process heat exchangers and is returned to the cooling tower. The heated water flows to the top of a tower, which is open to the atmosphere, and is allowed to flow down the tower over packing. Atmospheric

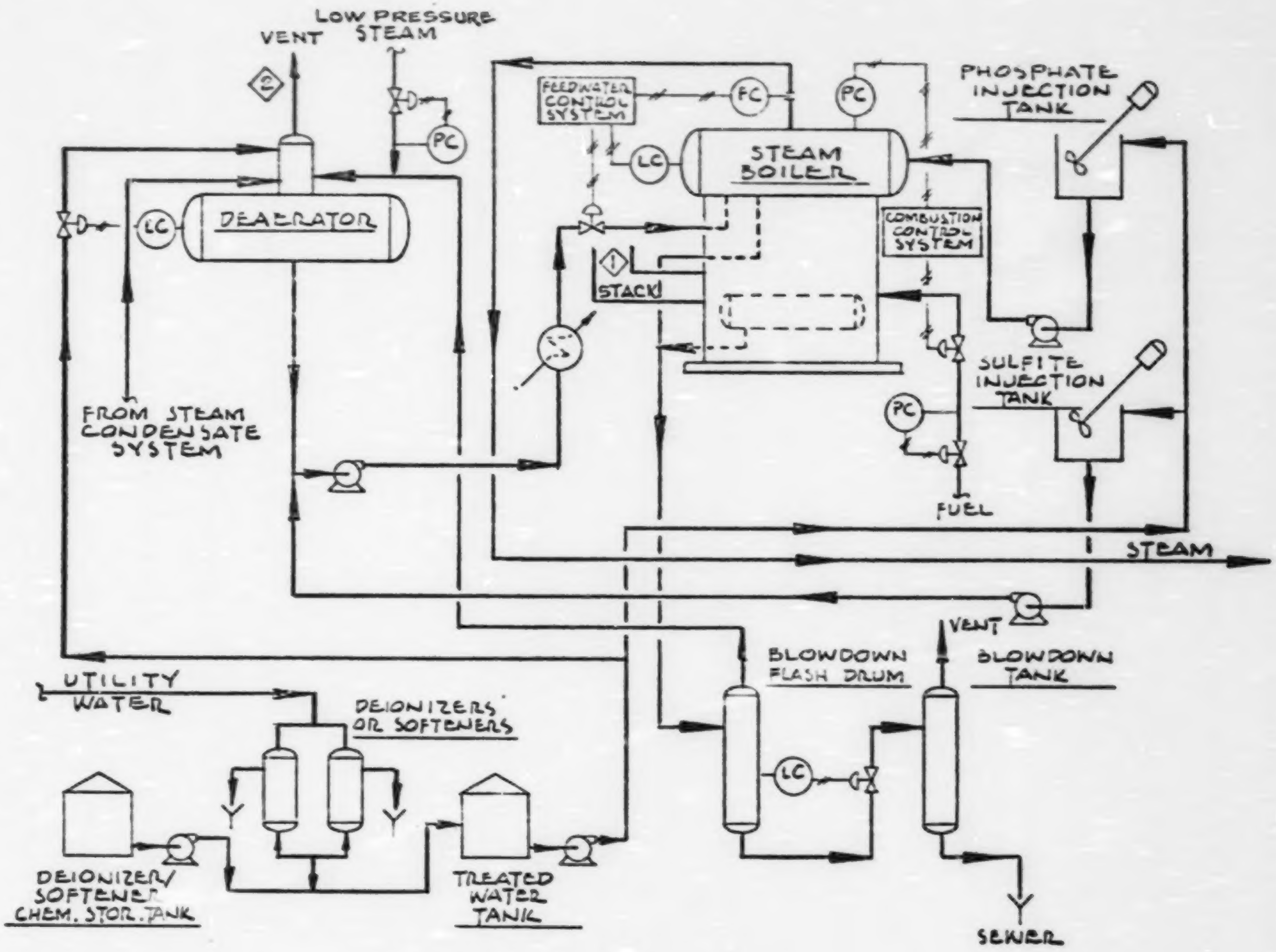

LOW PRESSURE STEAM
VENT
2
PC
DEAERATOR
LC
FROM STEAM CONDENSATE SYSTEM
FEEDWATER CONTROL SYSTEM
FC
PC
LC
STEAM BOILER
1
STACK
COMBUSTION CONTROL SYSTEM
PHOSPHATE INJECTION TANK
SULFITE INJECTION TANK
PC
FUEL
STEAM
VENT
BLOWDOWN FLASH DRUM
BLOWDOWN TANK
LC
SEWER
UTILITY WATER
DEIONIZERS OR SOFTENERS
DEIONIZER/SOFTENER CHEM. STOR. TANK
TREATED WATER TANK

Figure 42. Steam generation.

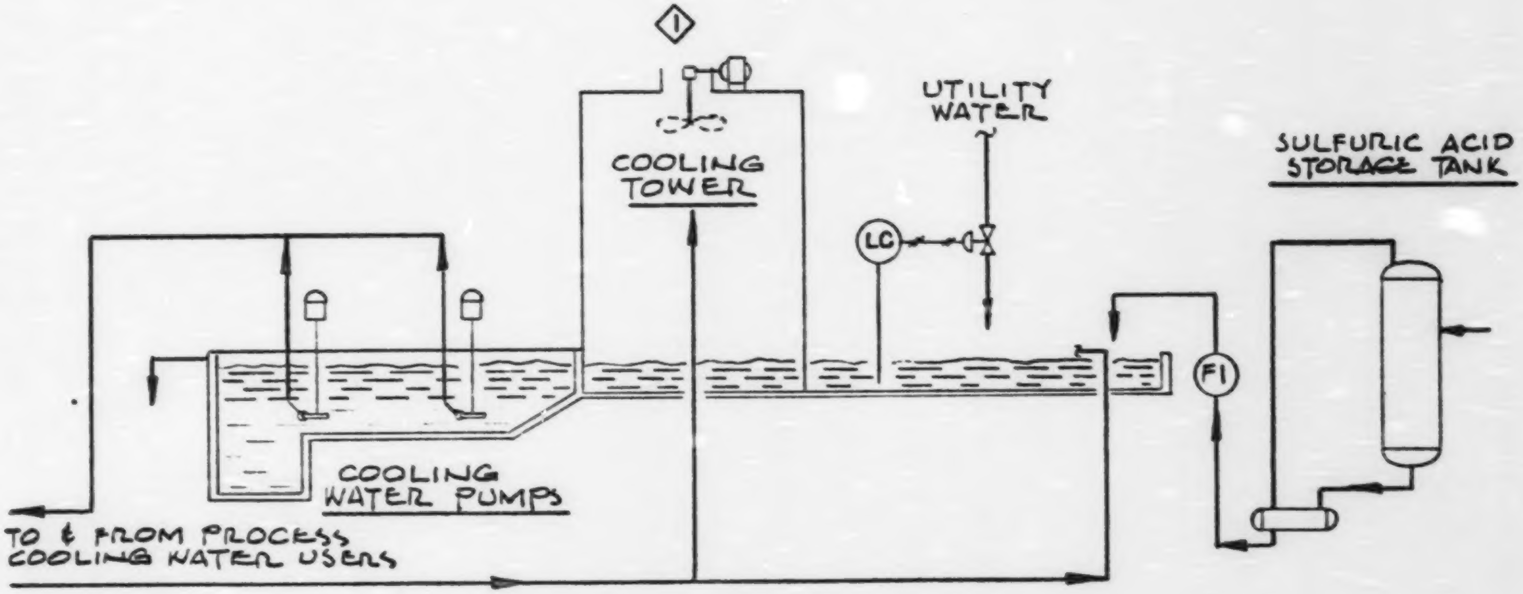

1
UTILITY WATER
COOLING TOWER
SULFURIC ACID STORAGE TANK
LC
FI
COOLING WATER PUMPS
TO & FROM PROCESS COOLING WATER USERS

Figure 43. Cooling tower.

air is either forced or flows by natural convection up the tower and the water is cooled by partial vaporization into the air flow. The cooled water is collected in the cooling tower basin prior to being pumped back to the process users. Utility water is added as make-up to the basin to replace water lost by evaporation in the tower, entrainment, and to blowdown. Chemicals, such as sulfuric acid, are added to maintain water quality.

The cooling tower (point 1 in the figure) could be the source of atmospheric pollutants if there is leakage of either hydrocarbons or other pollutants from the process side into the water side of a heat exchanger. Evaporation and entrainment losses can result in the release of significant quantities of pollutants into the atmosphere. A periodic check of the cooling tower basin for odor and visual surface contamination would indicate the presence of this type of leak.

AA. ELECTRIC POWER GENERATION

Each operation and process in an integrated refinery adds to the overall power requirement of the refinery. Requirements of the individual processes can vary from 0.3 to 5.0 kw of electrical power per daily barrel of throughput. Maintenance of adequate and reliable supplies of electrical power is a major concern.

Most refineries now use purchased electric power for normal operation. Commercial sources of power are reliable and power can be obtained at a reasonable cost. Refineries, however, frequently have emergency shutdown procedures that must be followed to prevent a major loss of product or damage to equipment in the event of a local power failure. Some pumps or blowers must continue to operate, and some instruments and alarms must be available to warn if a hazard exists. Normally, a refinery will have an emergency power generation system to meet this need. Emergency power generation equipment may be driven by steam turbine or by gasoline or diesel engine.

Remotely located refineries may not have access to a commercial source of power and may, therefore, generate their own power. The motive source to drive the main refinery generators may be a steam or gas turbine or a gas engine. The air pollution resulting from operation of gas turbines or gas engines is usually not excessive if low sulfur fuel gas is used. The air pollution characteristics of steam boilers are the same as those of other fired heaters (see Chapter II, Refinery Equipment).

BB. CATALYST REGENERATION

The catalyst in most of the refinery catalytic processes needs to be regenerated periodically. Whenever hydrocarbon feed stock is cracked, reformed, isomerized, or hydrotreated, some coke deposit will be formed on the catalyst and thus deactivate the catalyst. In most cases as soon as the catalyst gets partially deactivated, the yields decline and higher cracking or reforming severity is needed to achieve the desirable product characteristics. Higher severity in most cases means higher operating pressure and temperature which in turn deposits more coke on the catalyst. So at some point, the process has to stop and the catalyst has to be rejuvenated. The frequency of catalyst regeneration will depend upon the type of process, the feed stock and the severity of the operation. Regeneration frequency can vary between once every two or three years to once a week. In some processes, the catalyst bed may be removed, replaced with fresh catalyst and the deactivated bed shipped to be regenerated elsewhere. Most catalysts, however, are regenerated in place either continuously or periodically. For continuous catalyst regeneration, see the process description of catalytic cracking, especially fluid catalytic cracking.

Periodic in situ catalyst regeneration procedures are similar for most processing units. The only way coke can be removed without disturbing the catalyst bed is by burning it with air. Some processes may use steam and air to burn the coke while others can use inert gas (mainly nitrogen) and air when the catalyst is sensitive to water. The decoking operation will normally proceed as follows:

1. Purge and depressurize the reactor.
2. Inert gas or steam circulation.
3. Coke burning.
4. Inert gas and combustion products purge.
5. Gas purge and repressure.

The initial step is to cut off the feed to the reactor and purge the unit into the relief header and to the flare. At this stage, steam or inert gas (less than 0.1% O_2) may be added to the system and the purge will continue until all the volatile combustible materials are out of the system. Pockets of combustible material in the system could cause an explosion during the coke burning step. When the gas purge is clear of hydrocarbons or other combustible gases, the inert gas or steam is recirculated through a compressor and a heater to bring up the temperature of the catalyst bed to the coke ignition level. Some of the coke will break loose at this stage and flow out of the system with some catalyst dust. Both coke and dust have to be removed, for instance, by wet scrubbing. Also, if steam is used, some CO_2, CO and H_2 will be formed and some of the circulating gas needs to be continuously purged. At the preset temperature (500-700°F) air is allowed into the circulating inert stream, and the coke burn begins. Excess gases are continuously purged, and coke particles and dust are scrubbed out of the recirculating stream. The circulating gas temperature is allowed to go to about 1,000°F by regulating the amount of air allowed into the system. The "hot spot" where the coke burns slowly proceeds down the catalyst bed until all the coke deposit is consumed. At this point, the circulating gas is purged to the flare with fresh inert gas. This purge continues until the oxygen level in the system is reduced and the ash and dust are removed. The inert gas is then circulated to reheat the system to operating temperature and feed is introduced while the inert gas is purged to the flare.

Gaseous air pollutants are formed throughout the regeneration operation by the reaction of steam air and coke, and mechanical action forms dust. If sulfur is present in the coke, SO_2 will be formed as a part of the coke combustion products. Coke dust, ash, and catalyst dust also are present throughout this operation and have to be removed before the combustion gases are discharged to the atmosphere. Wet scrubbing of the purged gases with a caustic wash may be used in some cases to reduce the SO_2 and the dust in the combustion gases. However, this scheme is not in general use and cannot be used where water is a catalyst poison.

II. REFINERY EQUIPMENT

A. INTRODUCTION

In the same way that individual chemical processes have characteristic kinds of pollutant emission, the pieces of equipment used in these processes have characteristic points of pollutant emission.

This chapter contains a summary of the major types of process equipment and their performance characteristics. The internal mechanisms of each are illustrated. Emphasis is directed toward the mechanisms by which each item of equipment might release material to the atmosphere under normal and abnormal operating conditions.

The objective of this chapter is to provide sufficient information about process equipment so that the FEO will recognize the equipment, understand its function, and be sufficiently knowledgeable regarding its operation to decide whether the unit is being operated properly. If improper operation is evident, he should be able to recommend changes to the system that would reduce pollutant emissions to the point where the facility can comply with environmental pollution standards.

B. PUMPS

A refinery uses many different types of pumps to move fluids.

Pumps vary in capacity up to 100, 000 gallons per minute and in pressure differential up to 30, 000 pounds per square inch. A pump is designed to perform a specific function, and it is limited to a rather narrow range of operation above and below the design condition. For this reason, hundreds of pumps of different styles and modes of operation are used. The types most often used in refineries fall into two categories: centrifugal and positive displacement devices. Centrifugal devices are centrifugal, axial and turbine pumps. Positive displacement devices are reciprocating piston, plunger, diaphragm, rotary vane, and gear pumps. Other specialty pumps are available for unusual applications, but this list covers the types that will be encountered most often.

1. Centrifugal Devices

a. Centrifugal Pumps - A centrifugal pump consists of a rotating element, called an impeller, and a casing which surrounds the impeller. Liquid enters the pump and flows to the eye of the impeller. As the impeller rotates, it throws the liquid outward by centrifugal force. The casing collects the liquid that is discharged from the impeller converting a part of the kinetic energy in the liquid into fluid pressure. The centrifugal pump is a flow device which continuously imparts energy to a flowing fluid. Figure 44 is a cutaway view of a centrifugal pump.

The amount of energy imparted to the fluid is a function of the top speed of the pump impeller. The discharge pressure

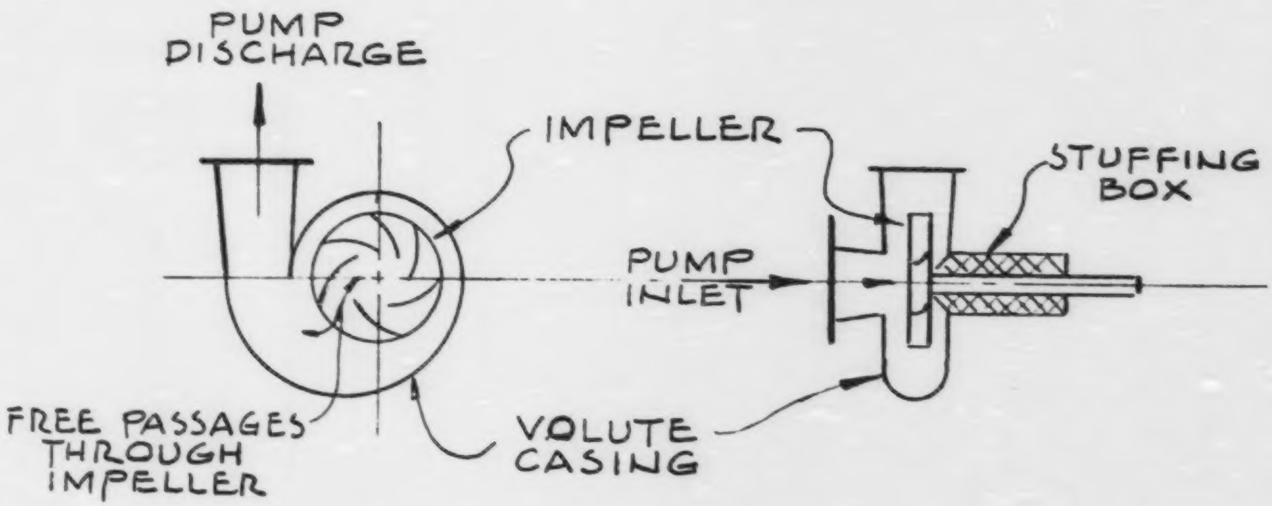

PUMP DISCHARGE
IMPELLER
STUFFING BOX
PUMP INLET
FREE PASSAGES THROUGH IMPELLER
VOLUTE CASING

Figure 44. Centrifugal pump.

of the pump increases with the diameter of the impeller and the speed of the pump. Low-pressure electrical pumps normally operate at 1, 750 rpm, and higher head pumps will rotate at 3, 500 rpm. Even higher pressures are available if a turbine drive is used to increase the impeller speed. Many different types of centrifugal pumps are used in the refinery. Figure 44 is typical of a single-stage, horizontal centrifugal pump. Where a high head is required, multiple impellers can be mounted on the same shaft as shown in Figure 45. The same type of pump is sometimes mounted in a vertical position to conserve space.

Figure 46 shows a sealed rotor, or canned motor, single-stage pump in which the rotor is exposed to the process liquid. The pump motor case is fully enclosed and therefore no seals are required for the pump. This pump is frequently used where the fluid pumped is particularly corrosive or toxic.

The centrifugal pump is a variable capacity pump. The liquid capacity of the pump can be regulated by adjustment of a valve on the discharge of the pump liquid. Closing the valve increases the head that the pump must provide, and the liquid capacity of the pump is reduced to meet the new requirement. As the valve is closed, the horsepower requirement of the pump is minimized. However, if the flow of fluid is stopped, the fluid in the pump will overheat and the pump could be damaged.

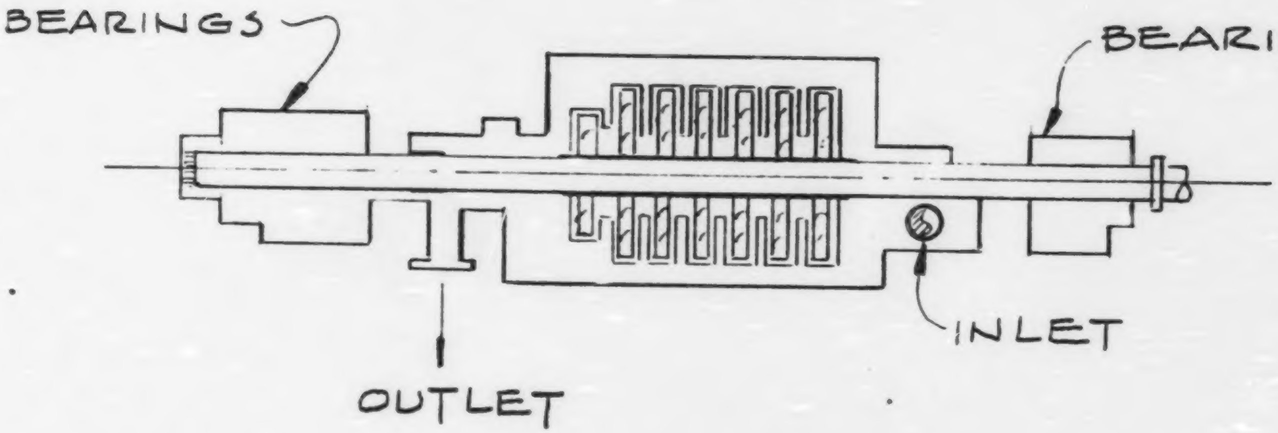

BEARINGS
BEARINGS
INLET
OUTLET

Figure 45. Multiple stage centrifugal pump.

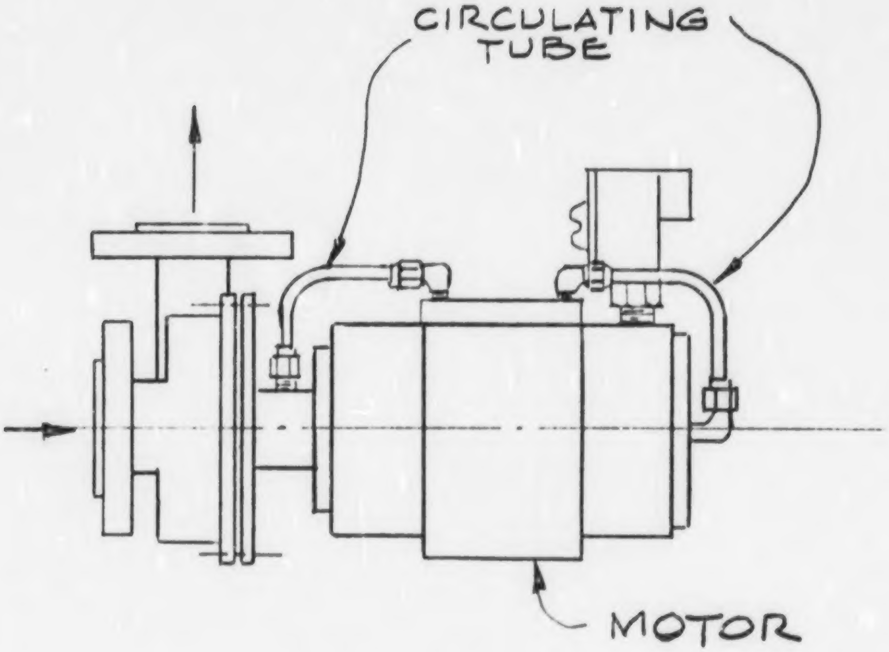

CIRCULATING TUBE
MOTOR

Figure 46. Canned motor pump.

The centrifugal pump shown in Figure 47 has three points where leakage might be expected to occur: at the inlet flange (point 1 in the figure), at the outlet flange (point 2), and at the shaft seal (point 3). If the system is properly constructed, the flanges will not leak and the principal spot where leakage will occur is at the shaft seal. The shaft seal may be a simple packed stuffing box which must be replaced periodically when leakage becomes excessive, or it may be a mechanical seal (see Figure 48). Mechanical seals work very satisfactorily and allow only minimum leakage with clean fluids, but deteriorate rapidly if the fluid contains abrasive particles.

Pump leakage is readily visible if the products do not vaporize. Where the liquid pumped has a high vapor pressure, vaporization will occur as soon as the product is released. Evidence of leakage may appear as an accumulation of condensate or frost around the point of leakage.

b. Axial Pumps - The axial pump uses both mechanical impulse and centrifugal force to pump large quantities of fluid where the head requirements are low. Figure 49 shows a section of a typical axial pump. The rotating element is a propellor, which is sometimes followed by stator blades to assist in recovery of the fluid energy.

Axial pumps are normally used for recirculation of fluids where the head requirement is low. One application is

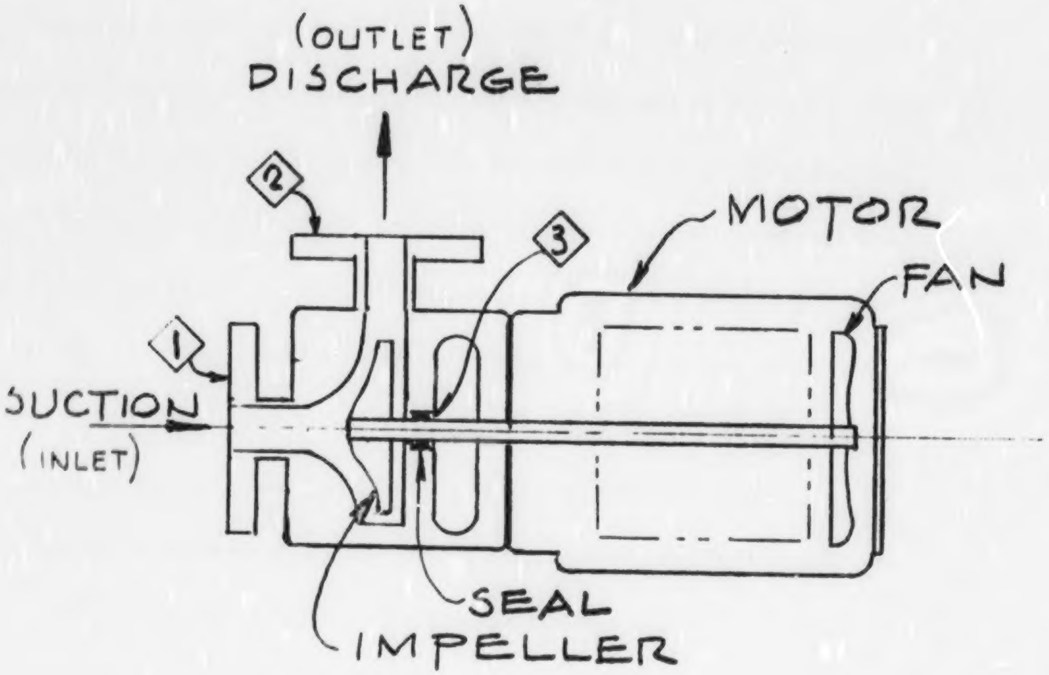
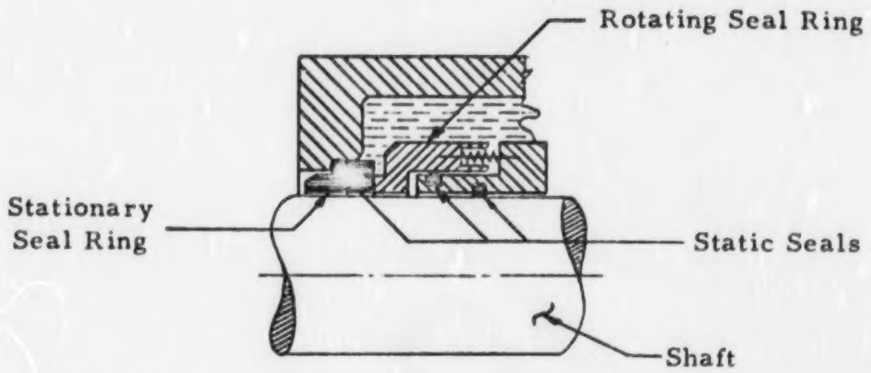
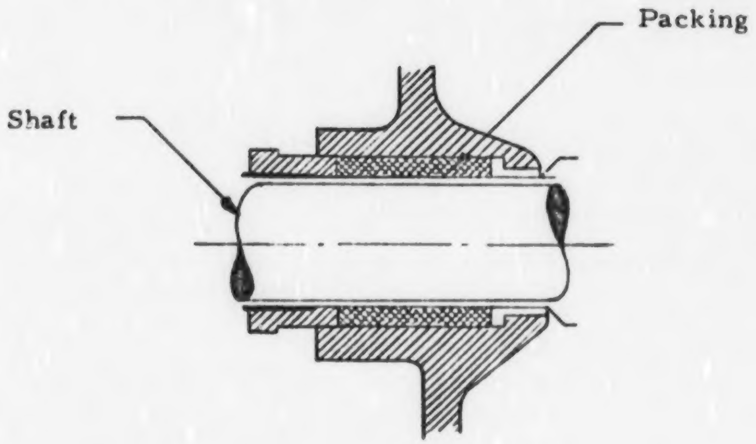

(OUTLET)
DISCHARGE
2
MOTOR
3
FAN
1
SUCTION
(INLET)
SEAL
IMPELLER

Figure 47. Close-coupled pump.


Rotating Seal Ring
Stationary Seal Ring
Static Seals
Shaft

Internal Mechanical Seal


Packing
Shaft

Packed Seal

Figure 48. Seals

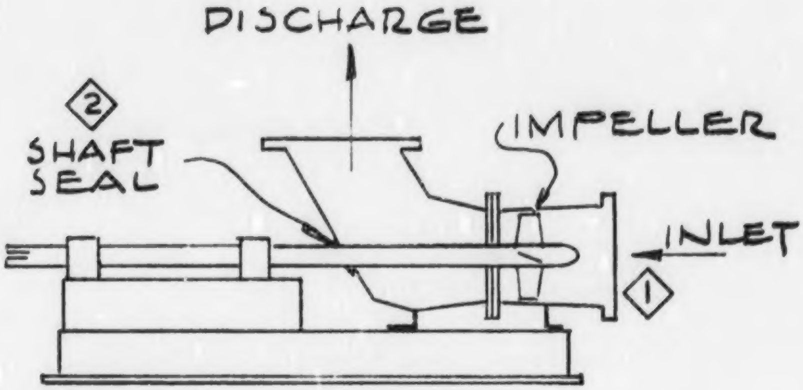

DISCHARGE
②
SHAFT
SEAL
IMPELLER
INLET
①

Figure 49. Axial flow propeller pump.
(elbow type)

in the circulation of large tanks of stocks such as gasoline. Side-entering mixers which are a type of axial pump are frequently used to obtain uniform blends of mixed stocks. If the discharge of an axial pump is throttled, the horsepower increases and the pump efficiency decreases. Normally these pumps are operated for maximum capacity with minimum regulation.

Hydrocarbon emission from axial pumps can occur at the points where the pump is connected into the system (point 1 in the figure) and at the shaft seal (point 2). Leakage at the shaft seal is most common. The discussion of the problem under the heading Centrifugal Pumps is also applicable here.

c. Turbine Pumps - Turbine pumps combine the characteristics of centrifugal and axial pumps. The impeller of a turbine pump, as shown in Figure 50, causes the liquid to move axially and radially as it passes the impeller. These pumps may have several stages in series and are frequently mounted vertically. They are often immersed in fluid to be pumped - for example, when they are used in wells.

2. Positive Displacement Devices

There are many pumps that move liquids by mechanical displacement of the liquid from a fixed chamber. These pumps are usually low-volume, high-differential pressure pumps. The capacity of the pump may be variable but is limited by the mechanical volumetric

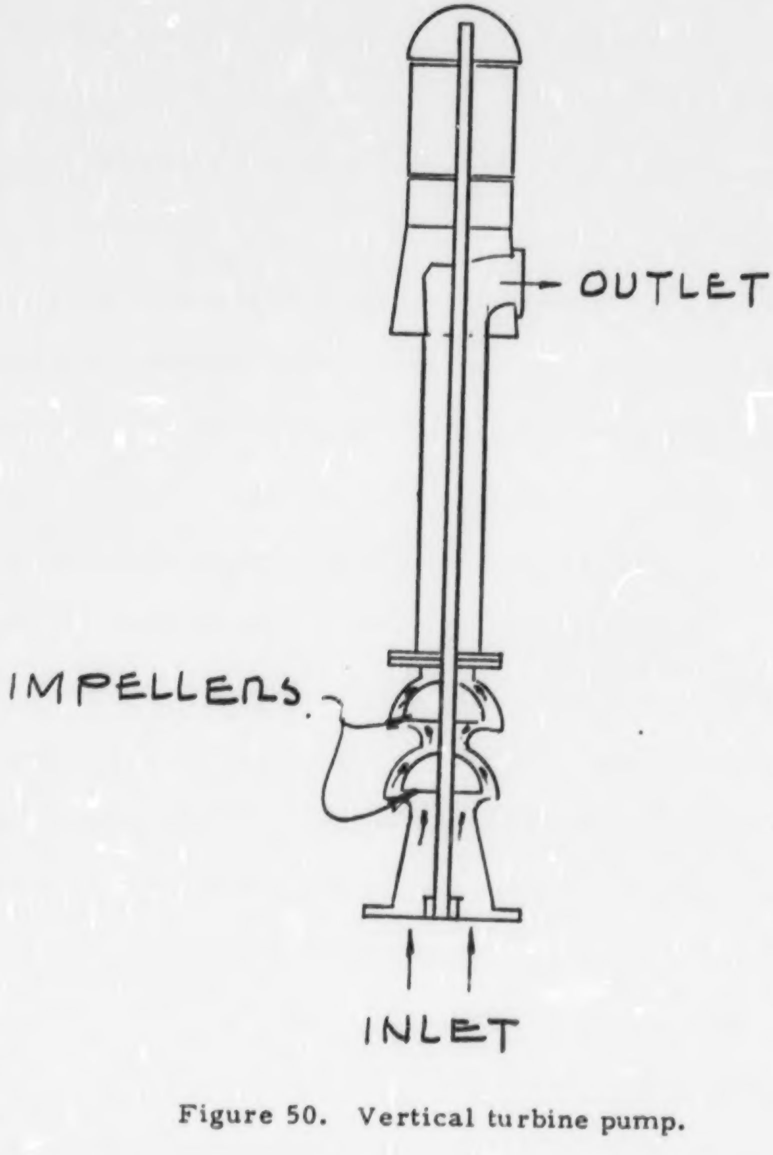

OUTLET
IMPELLERS
INLET

Figure 50. Vertical turbine pump.

displacement of the pump.

A positive displacement pump produces a discharge pressure that meets the head requirements of the system. The maximum head obtainable with the pump is fixed by the power limitations of the drive mechanism and it is not possible to throttle the discharge of the pump to adjust the fluid capacity. Instead, the rate of displacement of the pump must be adjusted.

a. Reciprocating Piston Pumps - The reciprocating piston pump is one of the oldest types of pumps in refinery service. Figure 51 shows a motor-driven piston pump which could be used to pump fluids in a high-pressure process system.

Each displacement stroke of a piston pump produces a flow pulsation. Some pumps are double acting, i. e., each movement of the piston causes fluid displacement to produce a more continuous flow. To smooth the flow even more, two or more pistons may be coordinated so that the flow pulsations are alternated. By these measures, the flow pulsations can be minimized until the flow is essentially continuous. Piston pumps are most susceptible to leakage through the packing on the pump shaft. This packing must slide along the shaft for the full stroke of the pump and is continuously subject to wear. To prevent excessive leakage, this packing should be regularly adjusted and maintained.

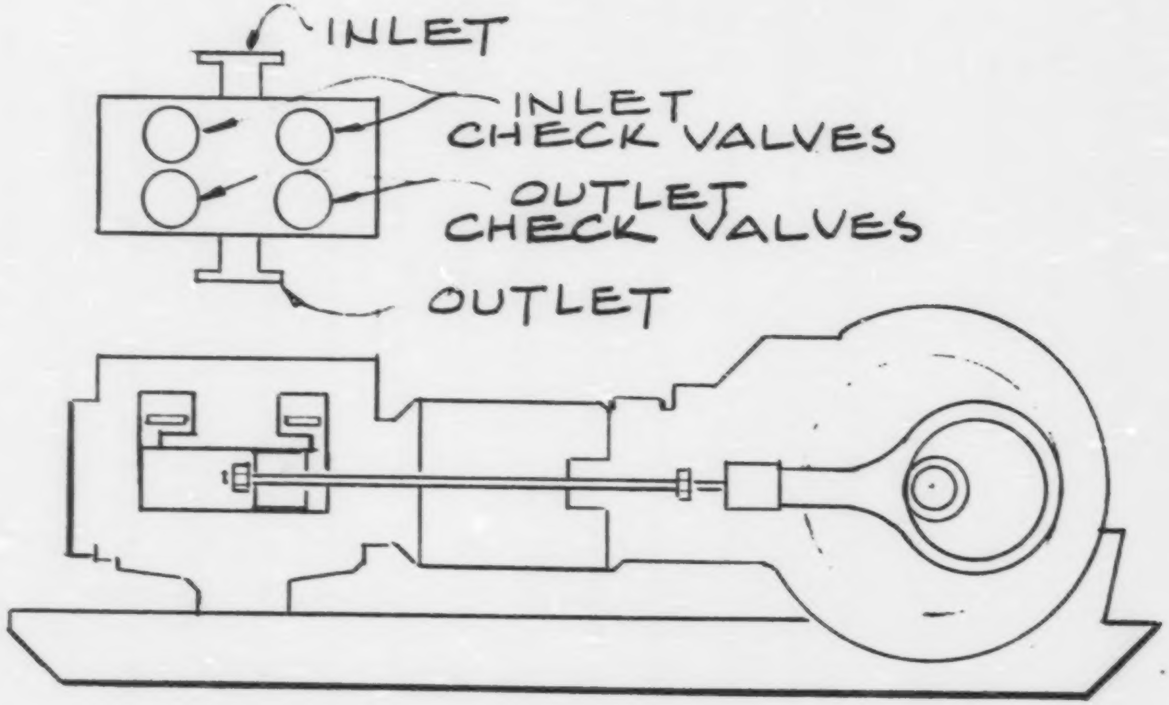

INLET
INLET CHECK VALVES
OUTLET CHECK VALVES
OUTLET

Figure 51. Reciprocating piston pump.
(double acting)

Piston pumps have check valves on the suction and discharge sides of each cylinder. These valves are subject to wear and must be serviced periodically. The valves are immersed in the fluid that is pumped and, to service the valves, this fluid must be removed. Removing it can release a significant amount of hydrocarbon to the atmosphere.

b. Plunger Pumps - Plunger pumps are similar to piston pumps in function, but instead of a piston they use a plunger which moves in and out of a fluid-filled chamber. A packed seal is used to prevent leakage around the plunger. The plunger punp is prone to leak through the packed seal in the same way that a piston pump leaks around the pump shaft. The valves of this type of pump must also be maintained regularly, and this operation could result in air pollution if not carefully performed.

c. Diaphragm Pumps - A diaphragm pump uses the movement of a flexible diaphragm to displace the fluid that is being pumped. Check valves on the inlet and outlet of the pump prevent the liquid from flowing backward. A typical diaphragm pump is illustrated in Figure 52.

The use of a diaphragm eliminates the need for a shaft or plunger packing to contain the fluid being pumped. However, the diaphragm itself is subject to failure and must be watched carefully. A leak in the pump diaphragm would allow the process fluid to escape to the atmosphere through the mechanism

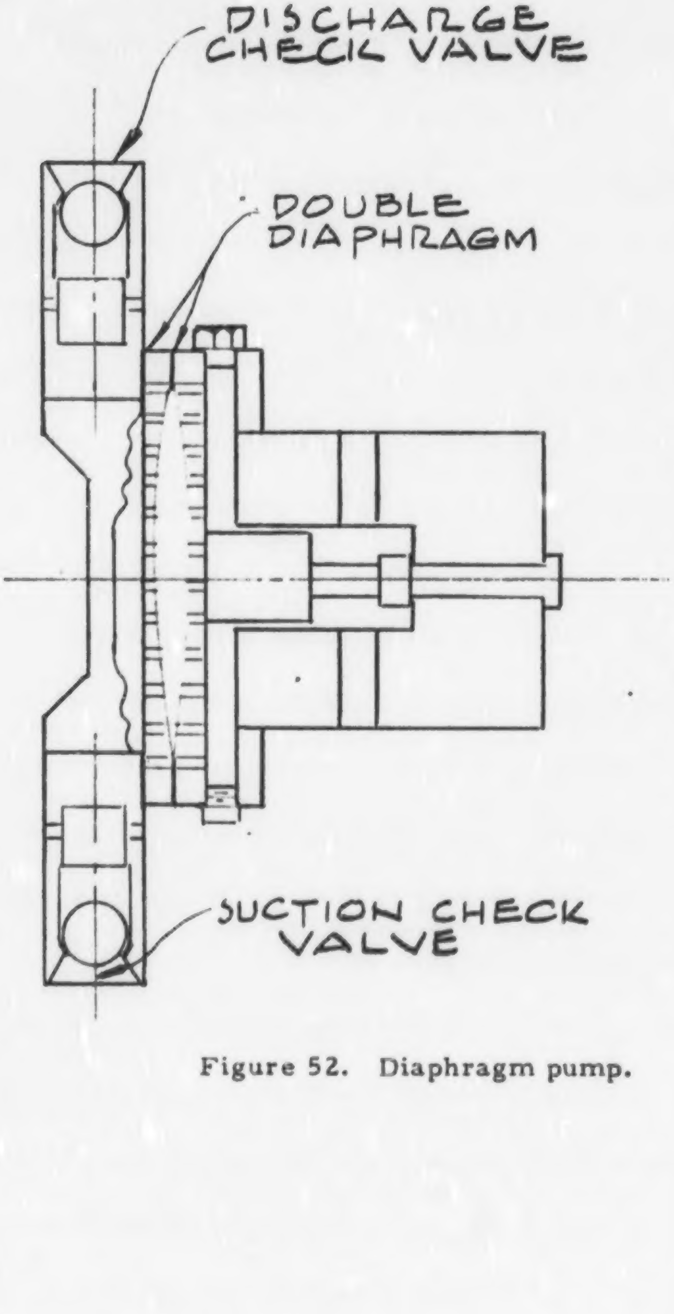

DISCHARGE CHECK VALVE
DOUBLE DIAPHRAGM
SUCTION CHECK VALVE

Figure 52. Diaphragm pump.

that is used to move the diaphragm.

d. Rotary Vane Pumps - Rotary vane pumps are frequently used at moderate pressures and temperatures to pump fluids. Figure 53 shows a cutaway drawing of a typical rotary vane pump. As the rotor turns counterclockwise, liquid is carried from left to right by the vanes which slide in and out of the slots in the rotor to maintain constant contact with the wall. The cylinder space is circular but it is offset from the axis of the rotor. Each revolution of the rotor moves a positive volume of liquid through the pump. The flow through the pump is non-pulsating, and the pump can handle fluids and gas without developing a vapor lock.

The shaft of this type of pump is the principal point of external leakage. However, effective shaft seals are available so that, with a well maintained pump, leakage should not be a problem.

e. Rotary Gear Pumps - Rotary gear pumps are used for low-head, low-capacity services with clean fluids. Figure 54 is a cutaway section of a dual-shaft, two-gear pump. As this pump rotates, the gear teeth carry fluid from one side of the pump to the other. The meshing teeth prevent the liquid from flowing backward.

The principal point of leakage with a gear occurs where the shafts penetrate the pump case. With a regular maintenance program, leakage at this point should be negligible.

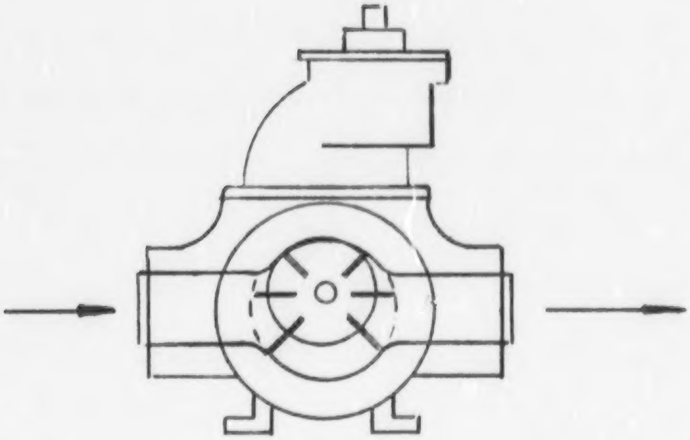


Figure 53. Rotary vane pump.

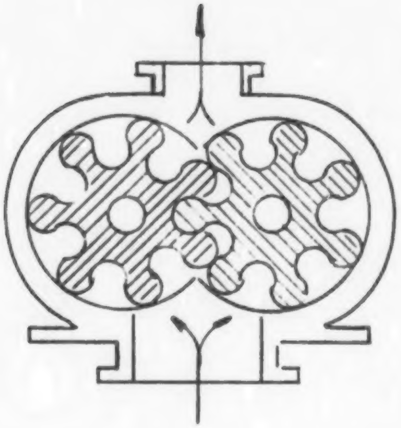


Figure 54. Rotary gear pump.
(two-impeller)

C. COMPRESSORS

Mechanical devices used to compress gases also fall into positive-displacement and centrifugal categories. Positive-displacement category includes piston, rotary-vane, and rotation-lobe compressors. The centrifugal category includes centrifugal and axial compressors.

The mechanism, used to drive the compressors, can sometimes become a secondary source of air pollution. Therefore the type of drive used with each compressor is also discussed briefly.

In addition to these devices, there are a number of hydraulic systems for compressing gas, but they are seldom found in refinery service and, therefore, are not discussed.

A unique type of gas-compression device which is described is the jet ejector, a simple device that uses the dynamic energy of one fluid to compress another.

1. Positive-Displacement Compressors

a. Reciprocating Piston Compressors - The reciprocating piston compressor is the most common type of gas compression device in use. It is used for pressure differentials from five to several thousand psi and for capacities from a fraction of a cubic feet per minute (cfm) up to the maximum capacity of a system. In refineries, reciprocating piston compressors are likely to be found in service compressing natural gas, hydrogen, or liquified petroleum gas (propane and butane).

Where pressure differentials are high, several stages of compression may be required to achieve a desired processing pressure. For high capacity gas compression requirements, several cylinders can be designed to operate in parallel. In many instances, a single multicylinder compressor may be used to compress two or more stages of several different gases.

For high-pressure systems most pistons are single-acting, two-stage devices as shown in Figure 55. At low pressure, the usual practice is to use double-acting pistons with a packed seal on each end of the piston rod. The cylinder is often supported by a sleeve or distance-piece and the crankcase is a second low-pressure packing designed to prevent loss of crankcase oil. Any gas which escapes from the cylinder is vented into the distance-piece, and in some cases, where the gas being compressed is toxic or flammable, the distance-piece is enclosed and a pressure vent to the flare is provided.

Large reciprocating gas compressors may be driven by electric motor or by gas or diesel-powered engine. Where a reciprocating combustion device is used to drive the compressor, the device could become a major source of pollution. The exhaust gas from such engines should be monitored as a part of the complete refinery inspection.

b. Rotary Lobe Blowers - Rotary lobe blowers are used for high capacity, low-differential pressure systems. A section of

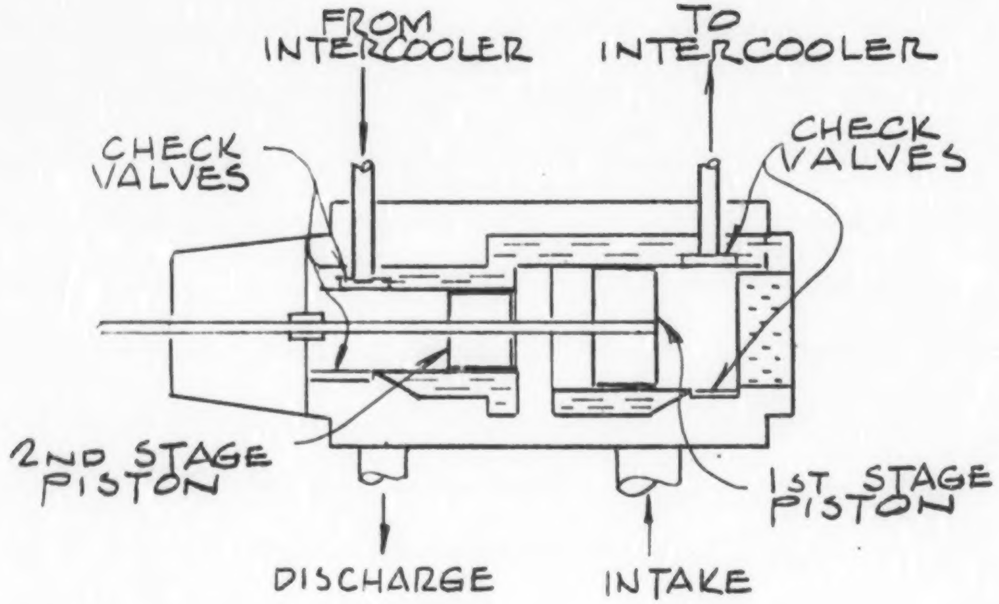

FROM INTERCOOLER
TO INTERCOOLER
CHECK VALVES
CHECK VALVES
2ND STAGE PISTON
1ST STAGE PISTON
DISCHARGE
INTAKE

Figure 55. Reciprocating compressor.
(2-stage)

such a blower is shown in Figure 56. Leakage occurs primarily at points where the shafts come through the case.

c. Rotary Sliding Vane Compressors - The rotary sliding vane compressor operates at relatively low pressures and capacities. As shown in Figure 57, a single rotor with sliding vanes turns in an eccentric cylinder, compressing the gas as it moves through the unit. As with the rotary lobe blower, leakage occurs primarily where the shaft comes through the case of the blower.

2. Centrifugal and Axial Compressors

Centrifugal and axial compressors may be used in various processes in the refinery. The centrifugal compressor is effective in compressing the relatively high molecular weight hydrocarbon gases. It is frequently used to compress the mixed gases from a catalytic cracking unit.

Axial compressors are suitable for high-capacity gas requirements, but they are not as versatile as the centrifugal compressor and have not been used extensively in refineries.

Figure 58 shows a centrifugal compressor shaft with a labyrinth seal used to prevent loss of gas. The seal consists of a number of restrictions and openings through which the escaping gas must flow. If this seal is not properly maintained, it can be a major source of loss of the process fluid. The labyrinth seal is normally vented at some midpoint and bled back to a lower pressure stage or to the compressor

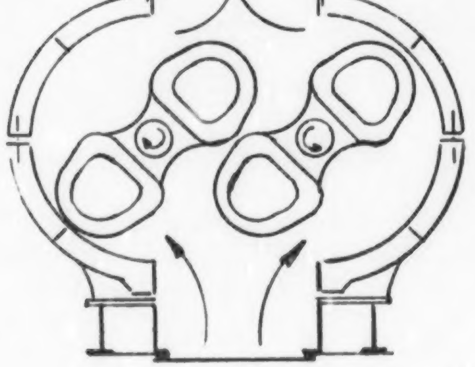


Figure 56. Rotary lobe blower.
(two impeller)

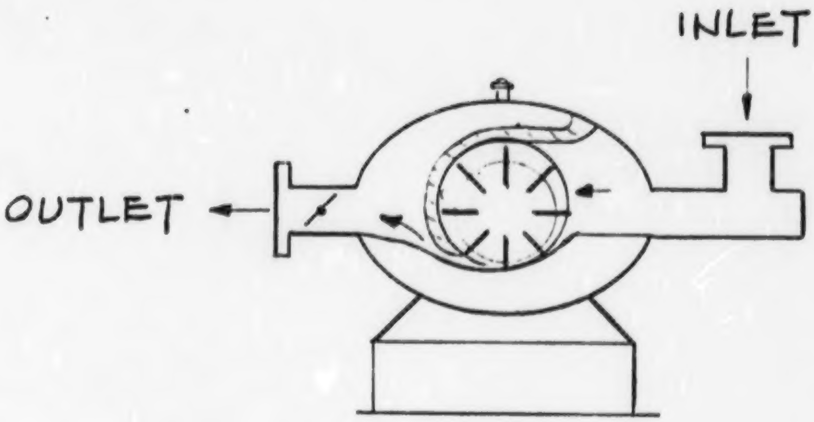

INLET
OUTLET

Figure 57. Rotary compressor.
(sliding vane)

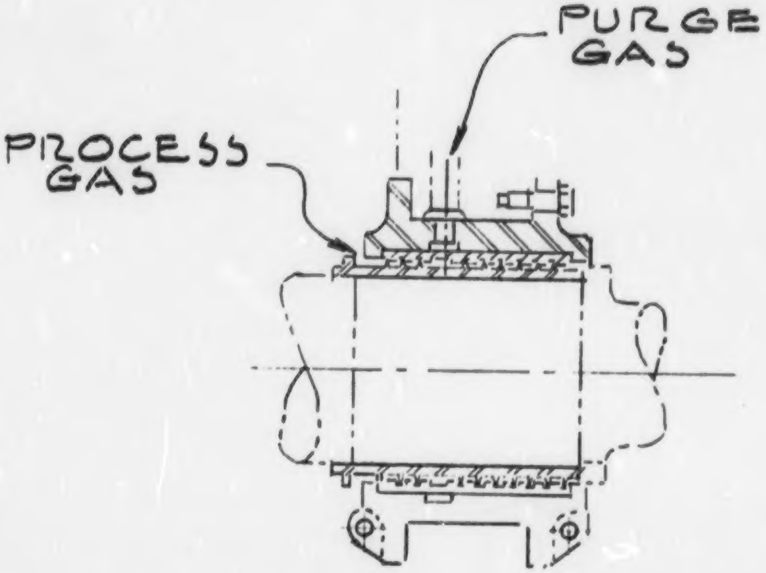

PURGE GAS
PROCESS GAS

Figure 58. Labyrinth seal.

suction. When loss of gas must be restricted, an inert gas or liquid can be injected into the seal at the midpoint of the labyrinth.

Centrifugal and axial compressors may be driven by an electric motor, a steam turbine, or a gas turbine. If a gas turbine is used, it could be a secondary source of pollution and, therefore, the exhaust gas from the turbine should be monitored.

D. HEAT EXCHANGERS

The exchanging of heat between refinery fluids is one of the methods by which heat is added or removed from refinery streams.

There are two types of mechanisms for effecting this exchange: the direct and indirect heat exchangers.

1. Direct Heat Exchangers

The single most important direct heat exchanger is the barometric condenser (Figure 59) used mainly for the condensation of steam in vacuum systems. Heat is exchanged by contacting the incoming steam directly with cooling water. The steam condenses and is pumped out of the system with the coolant. Noncondensables in this system are removed with a steam jet or a compressor.

Any pollutants in the steam will be distributed between the condensed steam and the noncondensables based on the degree of their solubility in water (point 1 in the figure). In most cases, however, the steam is relatively free of pollutants.

2. Indirect Heat Exchangers

Indirect heat exchangers are more common. In these units, the

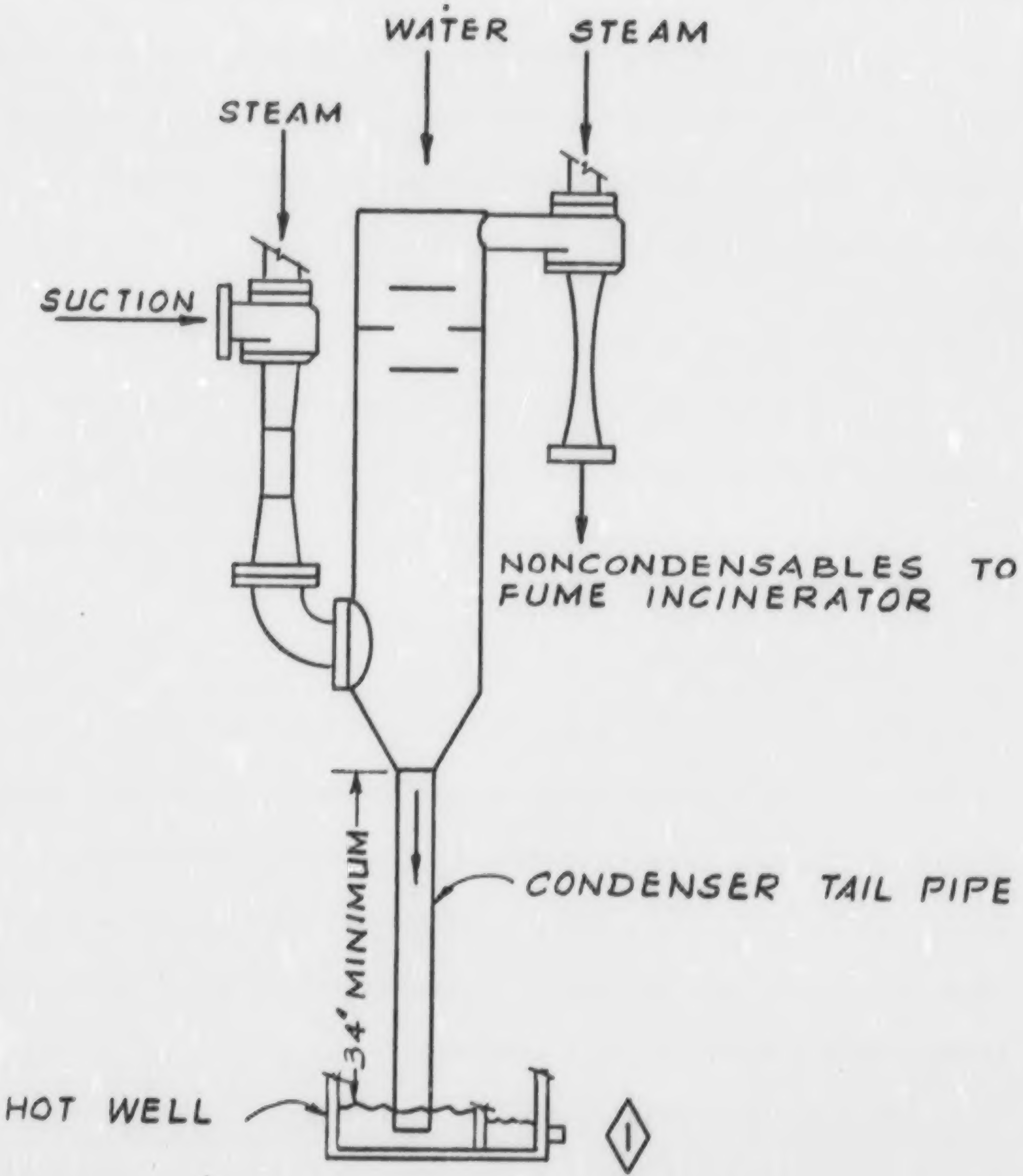

WATER
STEAM
STEAM
SUCTION
NONCONDENSABLES TO FUME INCINERATOR
34' MINIMUM
CONDENSER TAIL PIPE
HOT WELL
1

Figure 59. Barometric condenser.

two fluids exchange heat through a surface plate or a tube that separates them. This group of exchangers includes: the shell and tube, the double pipe, and the air-cooled.

Shell and tube heat exchangers (Figure 60) consist of a tubular shell 12 to 40 inches in diameter and 10 to 24 feet long with 3/4 or 1-inch in diameter tubes inside. One fluid thus flows in the shell and the other through the tubes.

A double-pipe exchanger (Figure 61) consists of two concentric pipes, one inside the other. The outer pipe may be 2 to 3 inches in diameter. The inner pipe is usually about 1 inch in diameter. The two fluids flow countercurrently through the two pipes, exchanging heat through the walls of the pipes.

Air-cooled heat exchanger (Figure 62) uses ambient air as the cooling medium. The fluid to be cooled passes through the inside of the tubes and a fan induces or forces a flow of air to the outside surfaces of the tubes. The fluid is cooled by transferring some of its heat through the walls of the tubes to the air. These units are relatively large, varying between 10 and 20 feet wide and 10 to 40 feet long. Often these units are stacked on top of and along the pipeway in the refinery.

Miscellaneous exchangers include plate coils, steam coils, tank heaters, and box coolers. Most of these exchangers are in steam heating, water cooling, or emergency services and are of little importance from the pollutant emission standpoint.

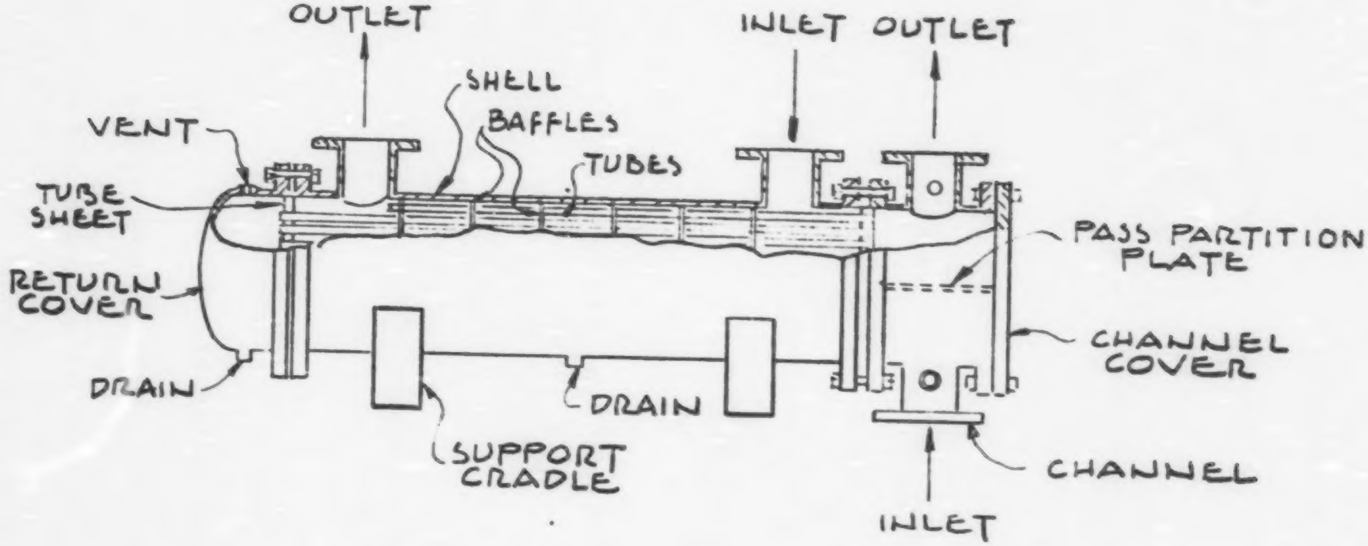

OUTLET
INLET
OUTLET
VENT
SHELL
BAFFLES
TUBES
TUBE SHEET
PASS PARTITION PLATE
RETURN COVER
CHANNEL COVER
DRAIN
DRAIN
SUPPORT CRADLE
CHANNEL
INLET

Figure 60. Shell and tube heat exchanger.

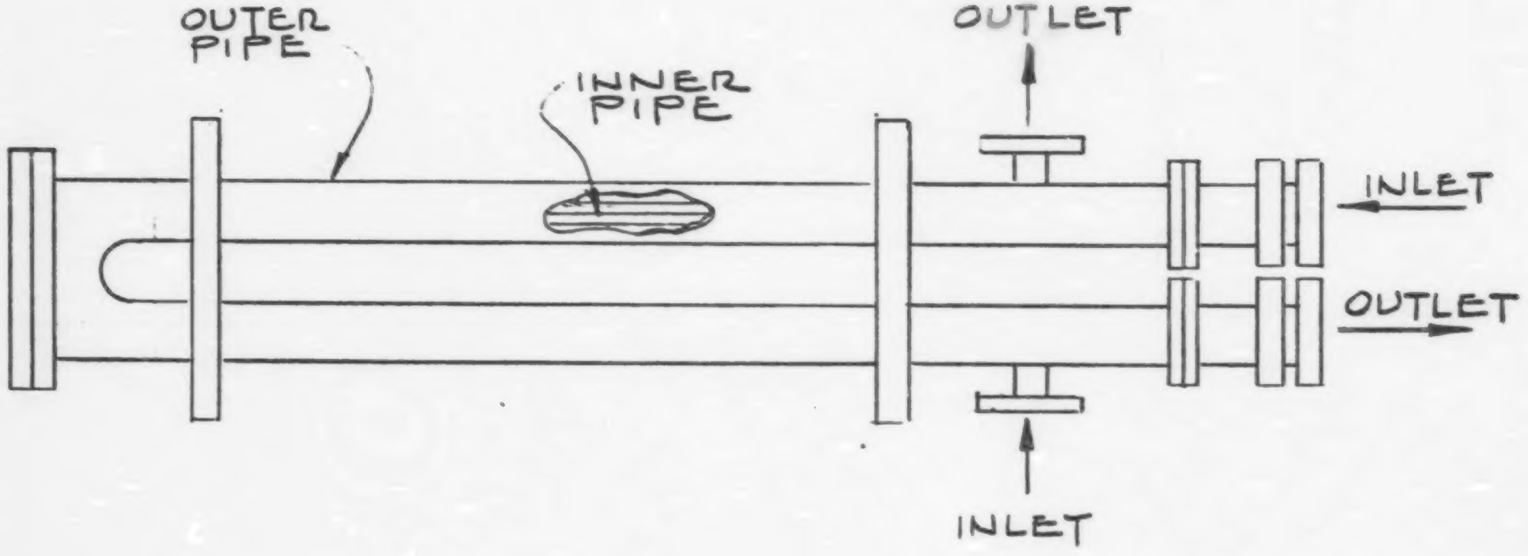

OUTER PIPE
INNER PIPE
OUTLET
INLET
OUTLET
INLET

Figure 61. Double-pipe heat exchanger with longitudinal fins.

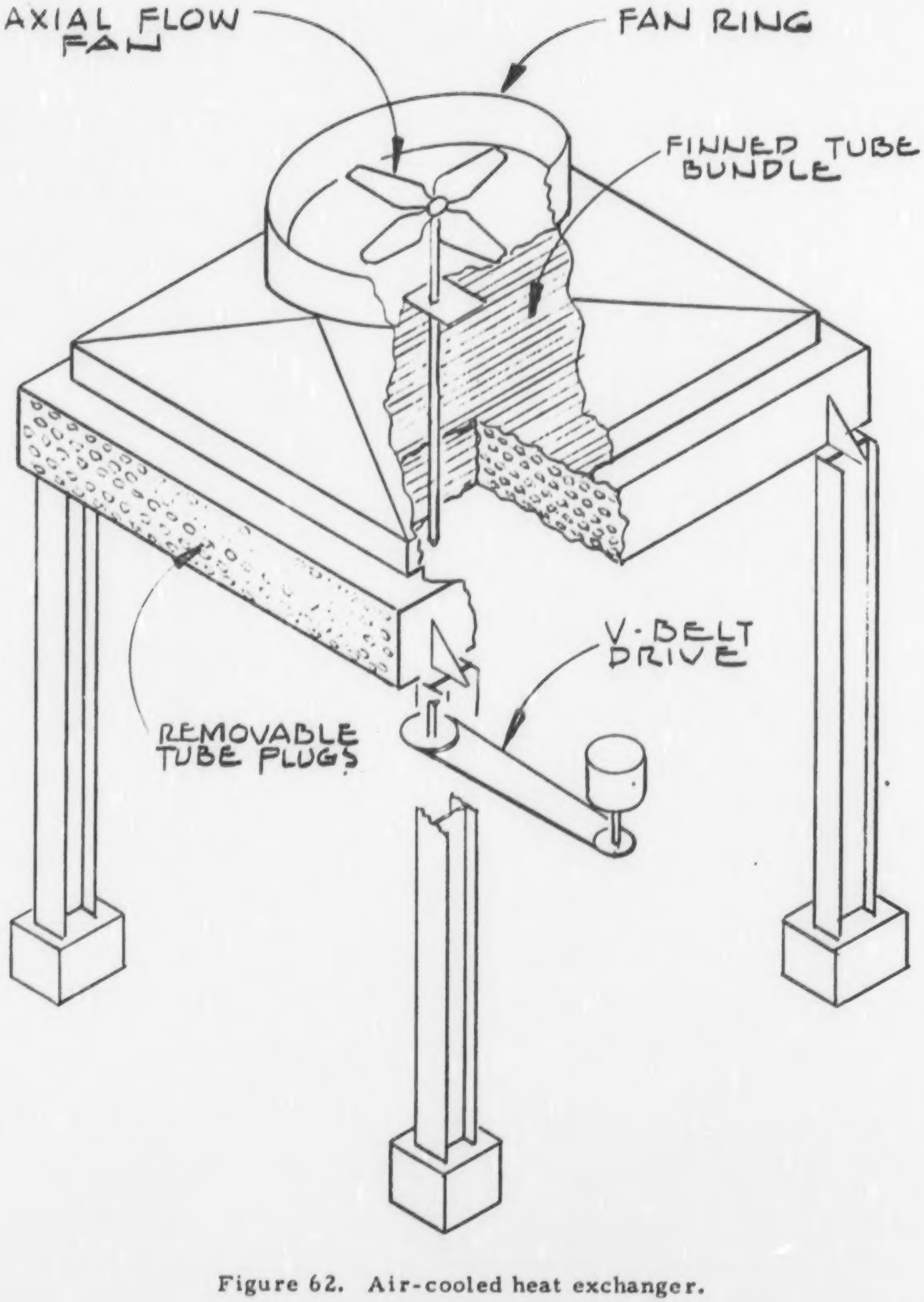

AXIAL FLOW FAN
FAN RING
FINNED TUBE BUNDLE
V-BELT DRIVE
REMOVABLE TUBE PLUGS

Figure 62. Air-cooled heat exchanger.

Heat exchangers normally do not emit pollutants. However, because of the corrosion of the tubes or leakage between the shell and the tubes, it is possible to contaminate the lower pressure fluid with the higher pressure fluid. When the lower pressure fluid is cooling water, the hydrocarbon contamination will be released in the cooling tower (see Section Z, Cooling Water System in Chapter I). If steam condensate gets contaminated with hydrocarbons, these contaminants will be released to the atmosphere with the noncondensables in the deaerator. By checking the composition of the effluent gas leaving the deaerator and the vapor leaving the cooling tower, leakage into the steam and cooling exchange systems can be detected. In some cases, leakage to the cooling water system can be detected by observing an oil film on the water in the cooling-tower basin.

E. FURNACES

Furnaces are used for heating refinery fluids. These units are also known as "fired heaters", "tube stills", or "pipe stills". In general, refinery process streams are heated by exchanging heat with other hot streams up to 400°F. When a process requires a higher temperature level or when other hot streams are not available, the direct-fired furnace will be used.

Refinery furnaces have many shapes and forms and varying firing and tube arrangements. Two of the more common units, the vertical cylinder and the horizontal box are illustrated in Figures 63 and 64.

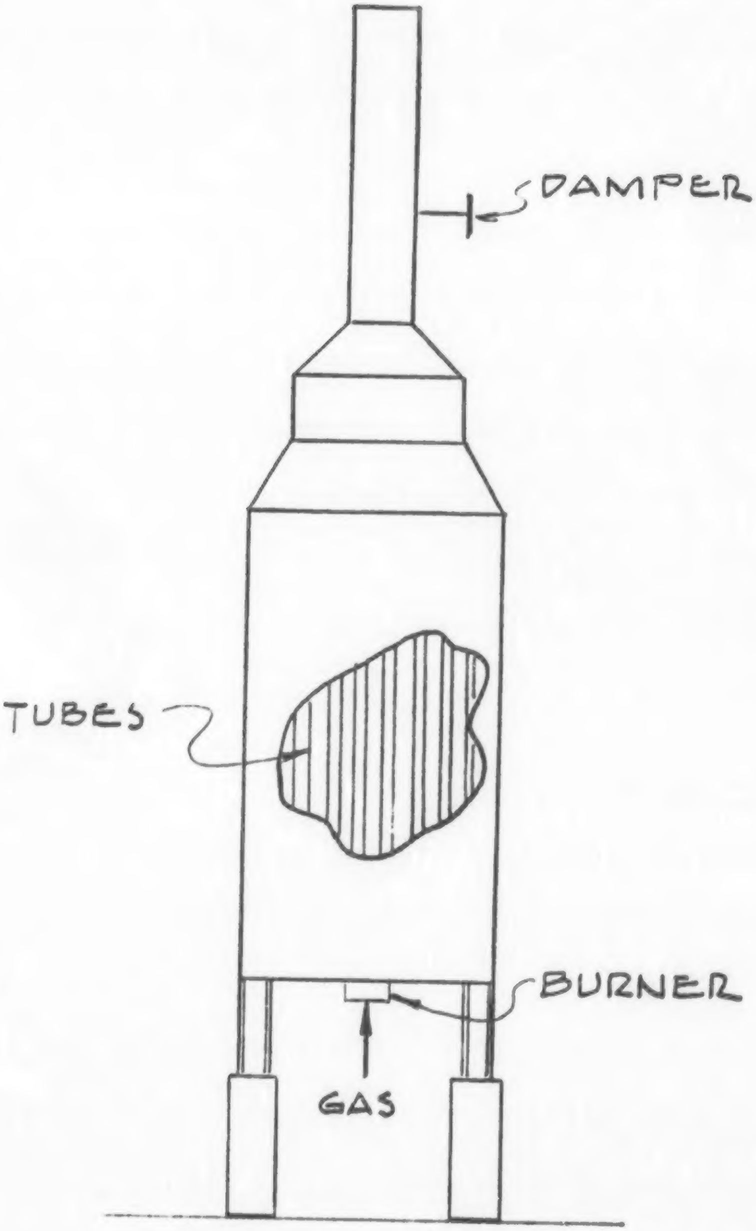

DAMPER
TUBES
BURNER
GAS

Figure 63. Vertical cylindrical furnace.

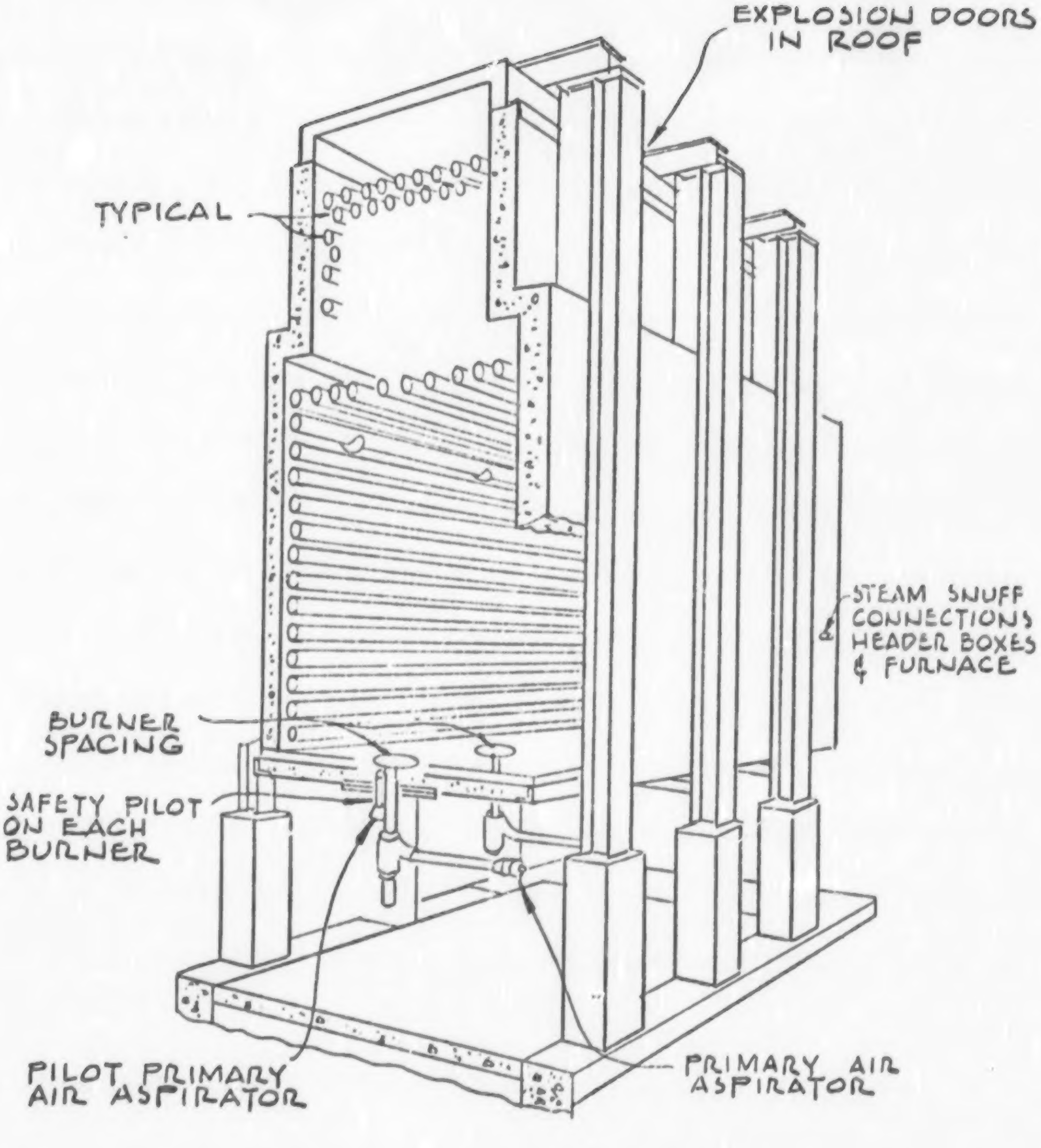

EXPLOSION DOORS IN ROOF
TYPICAL
STEAM SNUFF CONNECTIONS HEADER BOXES & FURNACE
BURNER SPACING
SAFETY PILOT ON EACH BURNER
PILOT PRIMARY AIR ASPIRATOR
PRIMARY AIR ASPIRATOR

Figure 64. Horizontal box type fired heater.

Most furnaces have two main sections: the convection section and the radiant section.

In the convection section, heat is exchanged between the hot combustion gases on the outside of the convection tubes and the process stream inside the tubes. Often additional tubes will be added in this section of the heater for superheating steam. The recovery of heat in this section greatly influences the total heater efficiency and reduces the stack flue-gas temperature. Flue gas temperatures in the stack vary between 500-700° F in an efficient heater and 900-1300° F in an inefficient furnace with reasonable amounts of excess air.

In the radiant section, heat is transferred to the tubes mainly by radiation. The refractory walls of the heater get red hot and emit heat. The tubes absorb this heat and transfer it to the process streams inside. The temperature of the walls in this section will vary from 1000 to 2000°F.

Fuel is delivered to the furnace through the burners. The function of the burners is to mix the fuel and the air, maintain a flame of proper shape, size, and stability, and ensure complete combustion. There are some 20 basic burner designs and many variations of each basic design.

A typical gas burner is shown in Figure 65. Natural gas or refinery gas is delivered to the burner at 3 to 20 psig. The fuel gas is mixed with the primary air, and the mixture is injected into the fire box of the furnace; the secondary air is drafted or forced through the air registers into the fire box where the combustion takes place. The

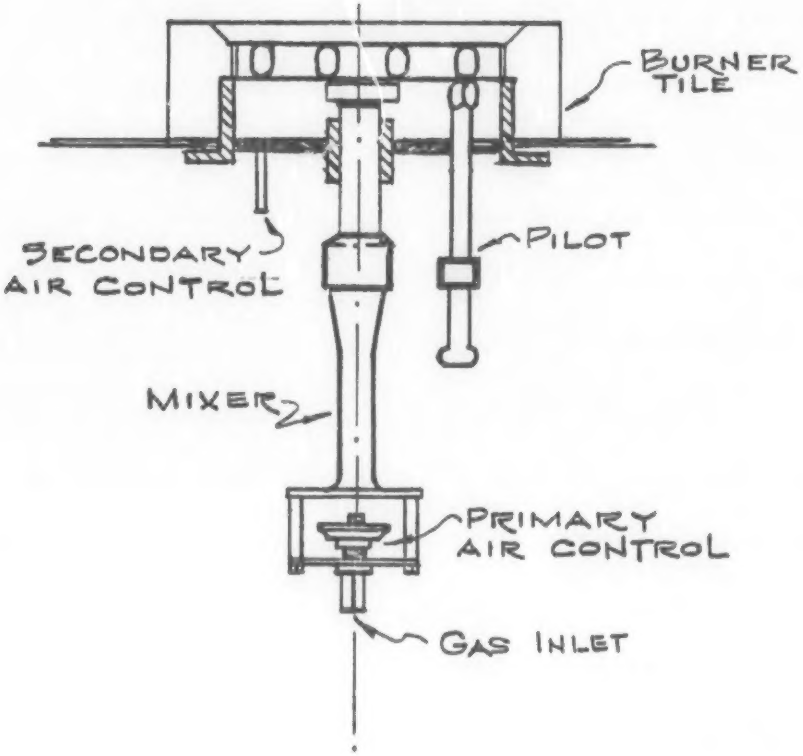

BURNER TILE
SECONDARY AIR CONTROL
PILOT
MIXER
PRIMARY AIR CONTROL
GAS INLET

Figure 65. Gas burner.

fire box is maintained at a low vacuum (up to 0.5 inches of water) and thus any flow of air is inward with little danger of the flame burning outside the firebox.

When heavy fuel oil is used for firing the furnace, the oil must be atomized, either by mechanical means or by steam. The combination oil-gas burner shown in Figure 66 is a steam-atomized fuel oil burner. The steam and fuel oil are fed simultaneously to the oil gun at about 100 psig. They form an emulsion like mixture in the oil gun, mix with the primary air, and are injected into the fire box much like the mixture in the natural gas burner.

The combustion product leaves the furnace through the stack. Stacks are designed to induce draft (low-level vacuum) in the fire box, dispose of the hot gases high enough above ground so that the fire danger is minimized, and reduce the ground-level concentrations of the combustion products. Both the burners and the stack create noise and may require mufflers.

Coke will deposit on the inside of the tubes when the furnace processes hydrocarbons. These deposits may be removed from the tubes either by mechanical cleaning (turbining) or by steam air decoking. The steam air decoking process is divided into two portions. First the tubes are heated by partial firing of the furnace to about 300°F and steam is allowed to flow through the tubes. The external heating of the tubes produces shrinking and cracking of the coke (spalling) inside the tubes and the steam blows the loose coke out of the tube.

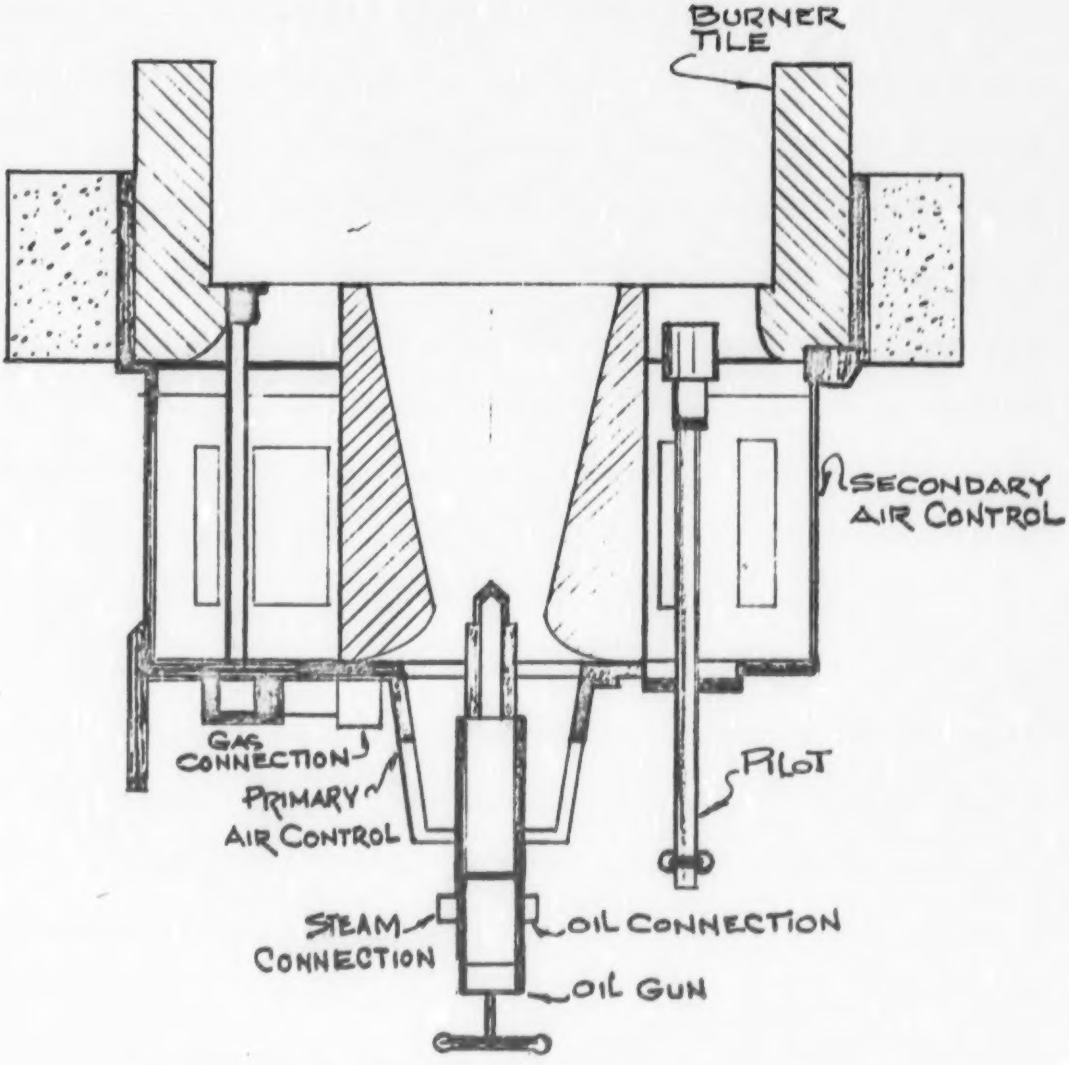

BURNER TILE
SECONDARY AIR CONTROL
GAS CONNECTION
PRIMARY AIR CONTROL
PILOT
STEAM CONNECTION
OIL CONNECTION
OIL GUN

Figure 66. Combination gas and oil burner.

Some of the steam will react with the coke to form CO_2, CO, and H_2. Coke particles, steam, and gases come out of the tube and into a concrete pit or drum; the decoking effluent is then cooled with water. All of the gases and most of the steam with some coke particles are discharged from the decoking drum into the atmosphere. When the spalling stops, compressed air is slowly added to the steam, and the coke deposits inside the tube start burning. The reaction of coke and oxygen produce CO_2 and CO. At this point, if any sulfur is present in the coke, SO_2 is formed. Current practice is to discharge the decoking effluents into the atmosphere. This may not be a severe problem if the furnace has to be decoked infrequently. Otherwise, flaring the effluents, or incineration of the gases in another furnace, may be required.

The emission of pollutants from furnaces is dependent on the fuel used for firing, the proper operation of the furnace, and - to a lesser degree - the design of the fire box and burners. Natural gas or refinery gas is the least polluting fuel if it is properly treated for the removal of all the sulfur components. All of the sulfur in the fuel oil or the fuel gas will be converted to SO_2 or SO_3 in the process of combustion.

Noncombustible residue in fuel oil, such as ash and metals, will be discharged into the atmosphere as soot and ash. Improper atomization of the fuel oil in the burner will produce unburned carbon in the flue gas. Refinery furnaces, in general, operate with high excess air

(15-25% excess air when gas fired and 30-50% excess air when oil fired). High excess air produces complete burning, reduces flame temperature, and minimizes the amount of carbon monoxide in the flue gas. However, high excess air reduces furnace efficiency. NO_x compounds are produced in the furnace from both the nitrogen in the air and the nitrogen compounds in the fuel. Only a very small portion of the nitrogen in air is reacted, while the generally accepted opinion is that most of the fuel nitrogen is converted to NO_x. Recent research on the formation of NO_x compounds in furnaces indicates that a reduced flame temperature can reduce the rate of formation of NO_x. Redesign of burners and fire boxes may be required in the future to reduce the flame temperature and with it the formation of NO_x.

F. JET EJECTORS

A jet ejector is a gas compressor that uses the dynamic energy of one fluid to compress another. The unit shown in Figure 67 consists of a nozzle, a vacuum chamber, and a diffuser tube. A high-pressure gas (normally steam) is expanded in the nozzle. It passes through the vacuum chamber at high velocity, entraining the surrounding vapor. The mixed gases then enter the diffuser where the kinetic energy in the gas is recovered as the gas decelerates, leaving the ejector at a pressure significantly higher than the pressure in the vacuum chamber.

A jet ejector can be used to move large amounts of gas from a low-pressure system to a higher pressure with a very low investment

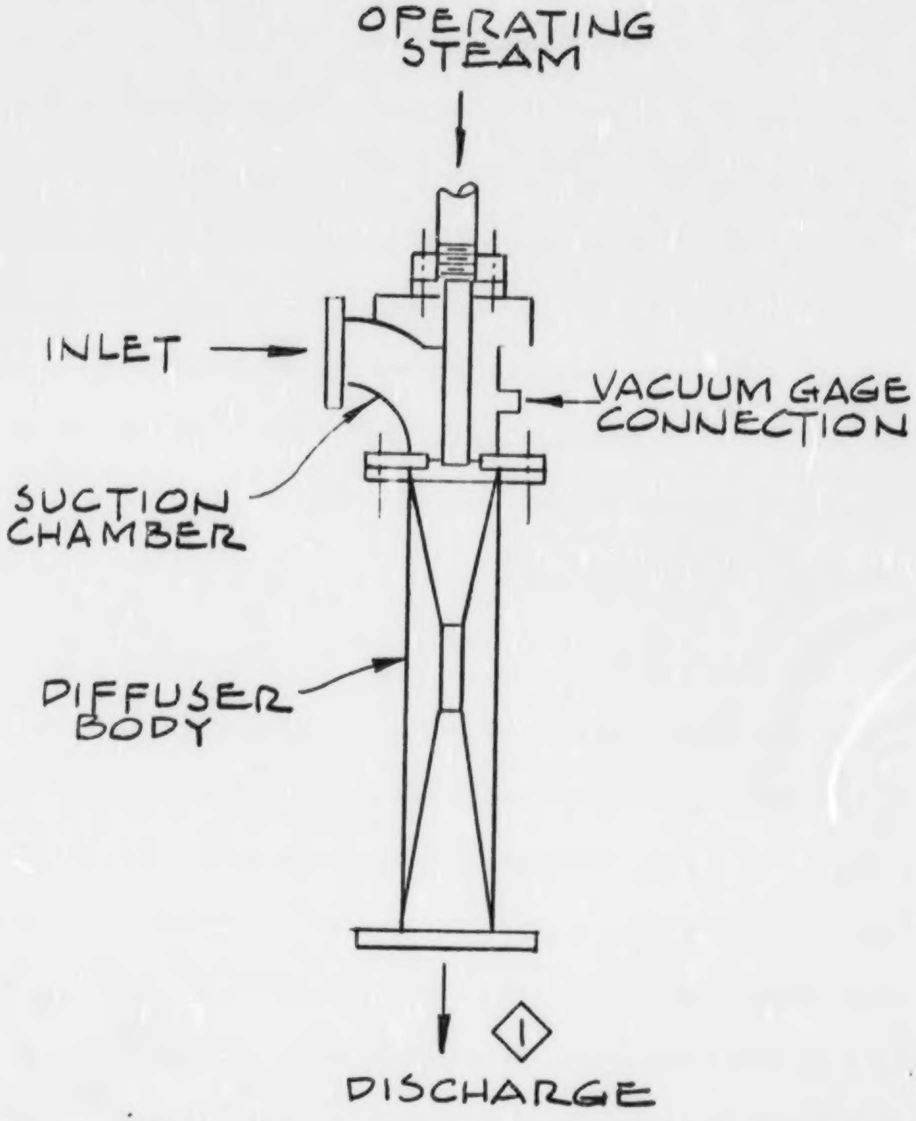

OPERATING STEAM
INLET
VACUUM GAGE CONNECTION
SUCTION CHAMBER
DIFFUSER BODY
1
DISCHARGE

Figure 67. Steam jet ejector.

in equipment. Consequently, ejectors are widely used in refineries in such services as tank evacuation, batch distillation, drying, and removal of inert gases from condensing operations.

The effluent gas from a steam-jet ejector consists of a mixture of process gas and steam. Frequently, these gases are discharged directly to the atmosphere (point 1 in the figure). If these gases contain significant amounts of hydrocarbon or sulfurous gases, this discharge could amount to significant pollutant emissions.

In many systems, the discharge from the jet ejector is cooled to condense the steam. The condensate removes some of the hydrocarbons and some of the acid gases such as H_2S. The condensate should be checked for sulfides and hydrocarbons and routed to the appropriate treating facility if they are present. The effluent gas from such a condenser should consist primarily of inert gases, but the vent gas should be analyzed to assure that the gases are being effectively scrubbed.

To obtain a high vacuum, two (or more) ejectors are sometimes connected in series. In some cases, an interstage condenser may be used to reduce the volume of gas to the second-stage ejector. The interstage condenser will operate at a reduced pressure and, therefore, will not be effective in absorbing acid gases and light hydrocarbons. Where these materials are present in the process gas, a condenser on the effluent of the second-stage ejector would be beneficial in reducing pollutant emission.

G. PIPE VALVES AND FITTINGS

1. Pipe

The pipe used in refineries in hydrocarbon service is primarily carbon and alloy steel. Carbon steel is used in ambient to moderate temperature service, and alloy steel is used in high-temperature service. In general practice, threaded connections are used for the smaller sizes (1-1/2 inches and under) and flanged connections are used for piping that is 2 inches and larger. Wherever possible, welded joints are used to connect sections of pipe to minimize leakage.

Specifications for pipe and fittings for refinery service are normally very conservative. It is reasonable to assume that if the pipe is in good condition, it will perform satisfactorily and will not contribute to atmospheric pollution. However, if the piping is allowed to corrode on either the interior or exterior surface, a significant reduction of wall thickness can occur with resultant leakage of the process fluid.

Threaded connections, when first assembled, can be made leak tight. However, if a threaded connection is assembled and disassembled many times, the threads become deformed and leakage becomes a probability.

Piping that is designed to hold very hot or very cold fluids must be capable of expansion or contraction. In some cases an expansion joint is installed in the line, but in most cases the line is designed with sufficient flexibility to absorb the change in length. Such lines are inclined to leak either at the expansion joint or at a terminal point in the line that is highly stressed by the pipe expansion.

2. Valves

A refinery uses many types of valves. Gate or ball valves are used where complete shutoff is required. Globe or plug valves are used where the valve is used for throttling or process control. Check valves are used in a flow line to prevent backflow. Control valves are used to regulate process flow.

All of these valves tend to leak through the valve seat when handling low viscosity fluids and/or when the pressure differential across the valve is large. Where a single valve is used to separate a material that is considered a pollutant from the environment, the outlet of the valve should be closed with a blind flange, a blind, or a plug, to assure that the material does not escape.

The second major source of valve leakage is the packing that is used to seal the valve stem. This packed joint must slide along the valve stem as the valve is opened and closed. A regular program of inspection should be scheduled to ensure that valve stem packings are properly maintained to prevent leakage to the atmosphere.

3. Flanges

Flanges provide a removable connection between pipe and vessels or other items of equipment. Flanges are specified by pressure rating and by facing. Pressure ratings used are: 150, 300, 400, 600, 900, 1500, and 2500 psi. The most common flange facings, shown in Figure 68, are flat face, raised face, tongue and groove, and ring joint. It is important that two opposing flanges have the same rating

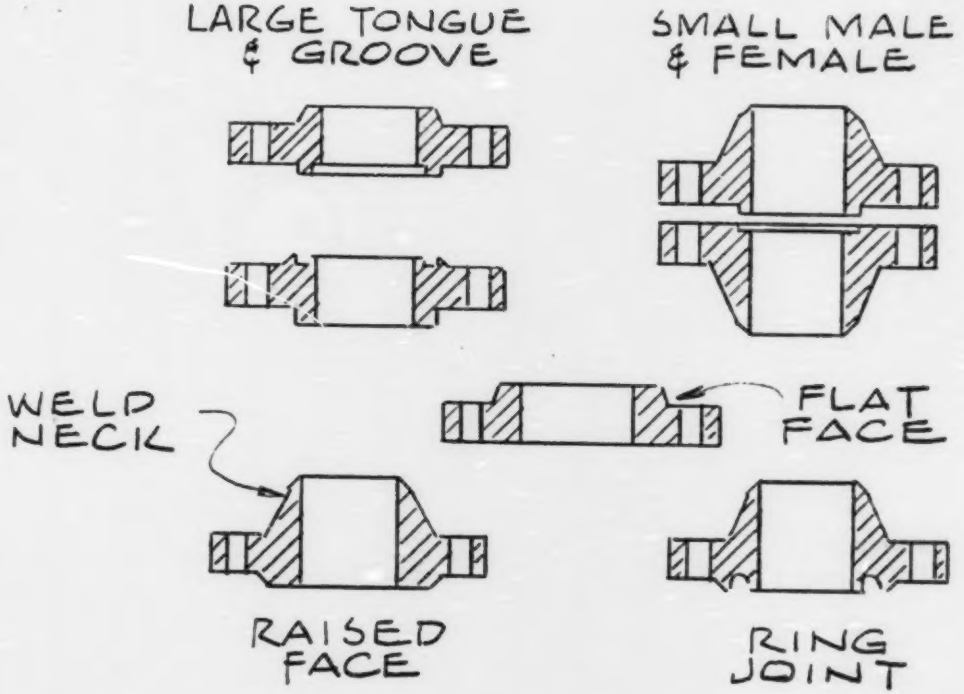

LARGE TONGUE
& GROOVE
SMALL MALE
& FEMALE
WELD
NECK
FLAT
FACE
RAISED
FACE
RING
JOINT

Figure 68. Flanges.

and facing. If mismatched flanges are connected together, there is a good possibility that the joint will warp and leak.

4. Vents and Drains

Most process piping is installed with vents on the high points of the lines and with drains at the low points of the line. These connections facilitate startup and shutdown procedures. They also constitute a prime candidate for leakage of the process fluid. Vent and drain connections on lines containing volatile hydrocarbons should be closed and sealed with a pipe plug or blind flange to assure that no leakage will occur at those points.

Many vessels containing hydrocarbons are equipped with manual drain valves which can be used to separate water from the hydrocarbon that is in the vessel. In this operation, an operator is supposed to visually observe when the water flow stops and the hydrocarbon flow starts. At this time the valve should be shut to minimize loss of hydrocarbon. Unfortunately, such manual separation operations are frequently left unattended, with the result that large quantities of hydrocarbon are dispersed into the environment.

H. PRESSURE-RELIEF DEVICES

All vessels, tanks, heat exchangers, and other equipment capable of being pressurized should be equipped with pressure-relief devices that will protect them from too much pressure. Many different types of pressure-relief devices are used for this purpose. The principal types of relief devices that may be encountered in a refinery are the spring-loaded relief valve, the rupture disc, and the relief hatch. Each device has different operating characteristics and failure modes. Knowledge of these characteristics will permit the FEO to determine if a given device is performing effectively.

Relief devices may be installed for relief of gaseous or liquid pressure. The liquid relief devices are normally installed to relieve thermal expansion and are less inclined to leak than vapor relief devices. Vapor relief devices are emphasized in this discussion because they are the primary source of pollutant emissions.

1. Spring-Loaded Relief Valve

A typical spring-loaded relief valve is shown in Figure 69. Fluid pressure is maintained in the throat of the valve. If the operating pressure exceeds the valve set pressure, the valve will open and relieve the system pressure.

Relief valves may discharge into a closed flare system or directly to the atmosphere depending on local air pollution regulations. If the discharge from the valve goes to a flare system, then leakage through the valve does not constitute pollutant emission. However, if the relief valve discharges to the atmosphere, significant amounts of material could be dispersed.

Relief valves, as delivered from the manufacturer, are normally gas-tight. However, after the valve has been actuated one or more times, it is possible that the valve may leak. In an effective refinery

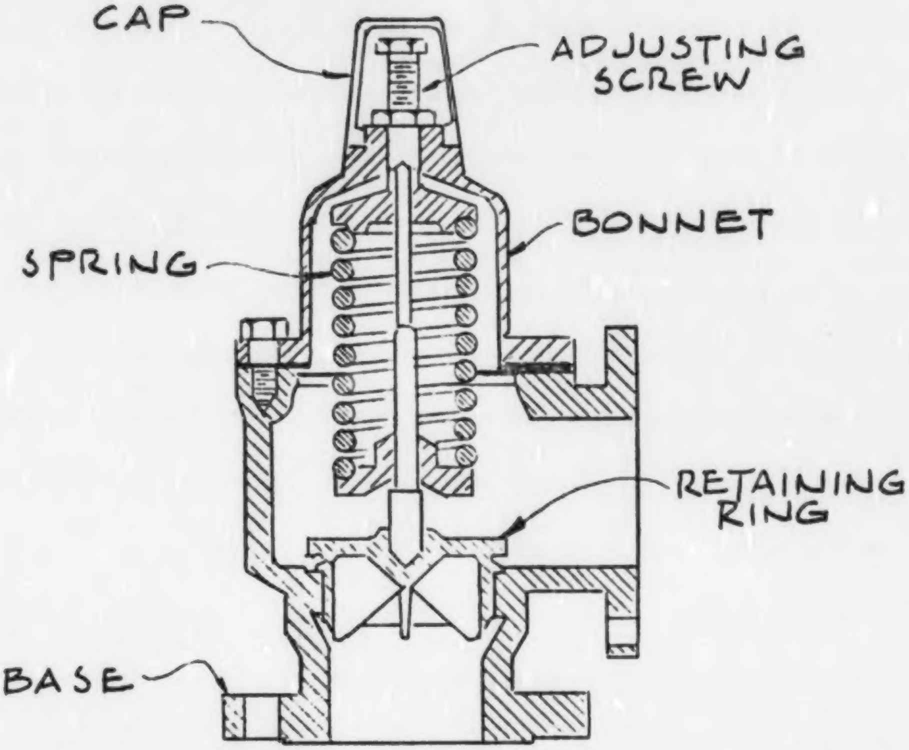

CAP
ADJUSTING SCREW
BONNET
SPRING
RETAINING RING
BASE

Figure 69. Relief valve.

maintenance program, all relief valves would be removed and checked for performance and leakage at least once a year.

Most relief valves achieve a seal by forcing a metal plate against a metal seat. These seats are durable but tend to leak. A more effective seal can be achieved by use of an "0" ring or plastic seat where process conditions permit their use.

Relief valves are normally set to activate at a pressure that is 10% or 25 psi above the normal operating pressure of a vessel. If the operating pressure is too close to the set pressure, the valve will tend to lift off the seat during normal operating cycles with resultant discharge of material through the valve and possible damage to the valve seat. The set pressure of each valve should be reviewed in relation to the operating pressure of the system to assure that the two pressures are separated sufficiently to prevent loss of material.

2. Rupture Disc

The rupture disc or burst diaphragm is a metal diaphragm which is designed to rupture at a predetermined pressure. Figure 70 shows a typical rupture disc assembly. The rupture disc is used to protect systems which might experience a sudden pressure rise or which must vent large quantities of gas in a short time.

In continuous processes, use of the rupture disc is limited because the entire system must be depressurized to replace the disc. Rupture discs are usually used on batch systems which can be readily shut down.

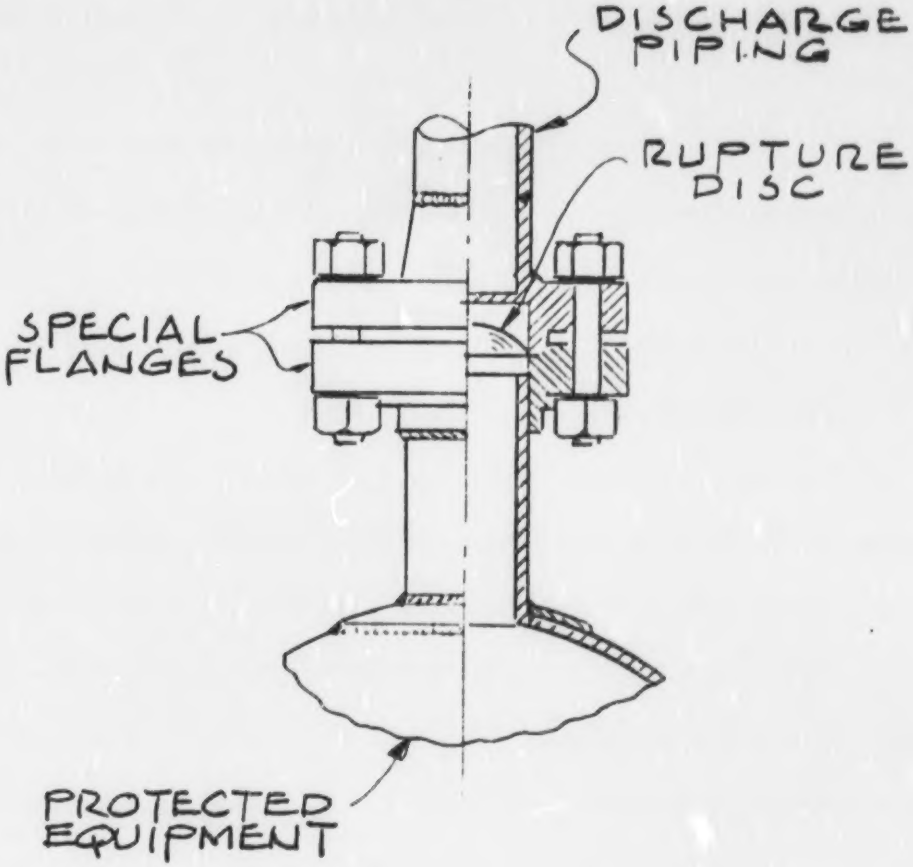

DISCHARGE PIPING
RUPTURE DISC
SPECIAL FLANGES
PROTECTED EQUIPMENT

Figure 70. Typical rupture disc installation.

Rupture discs can provide a vapor-tight seal when initially installed. However, it is possible for the disc to develop a pinhole leak due to atmospheric or internal corrosion. If such a leak should develop, significant amounts of material could be lost before the leak is discovered.

The effluent from a rupture disc may be vented directly to the atmosphere or it may be discharged into a flare system. Rupture discs which discharge directly into the atmosphere should be checked frequently for leakage.

3. Relief Hatch

The relief hatch is designed to provide a large emergency relief opening for handling large volumes of vapor at low pressure or in case of internal explosion. Figure 71 is a typical section of such a device.

These relief devices normally discharge directly to the atmosphere. If the device becomes warped or if the gasket surface deteriorates, significant quantities of material may escape to the atmosphere.

I. FLARES

The primary purpose of a flare is the safe disposal of waste gases by combustion. Except during rare emergencies, it should be possible to accomplish the complete combustion of the waste gases without producing smoke or noise.

The flare shown in Figure 72 is representative of one of a number of acceptable designs. It is an elevated flare with a smokeless tip.

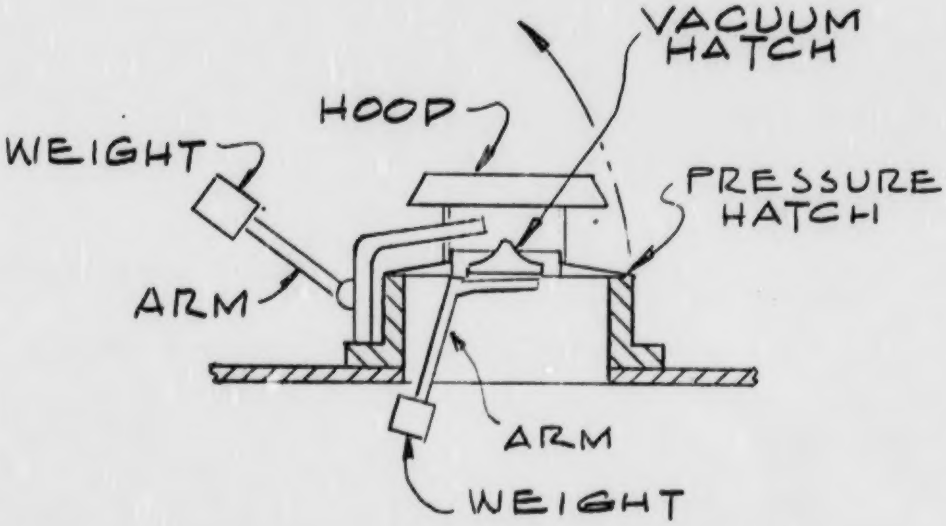

VACUUM HATCH
HOOP
WEIGHT
PRESSURE HATCH
ARM
ARM
WEIGHT

Figure 71. Pressure relief hatch.

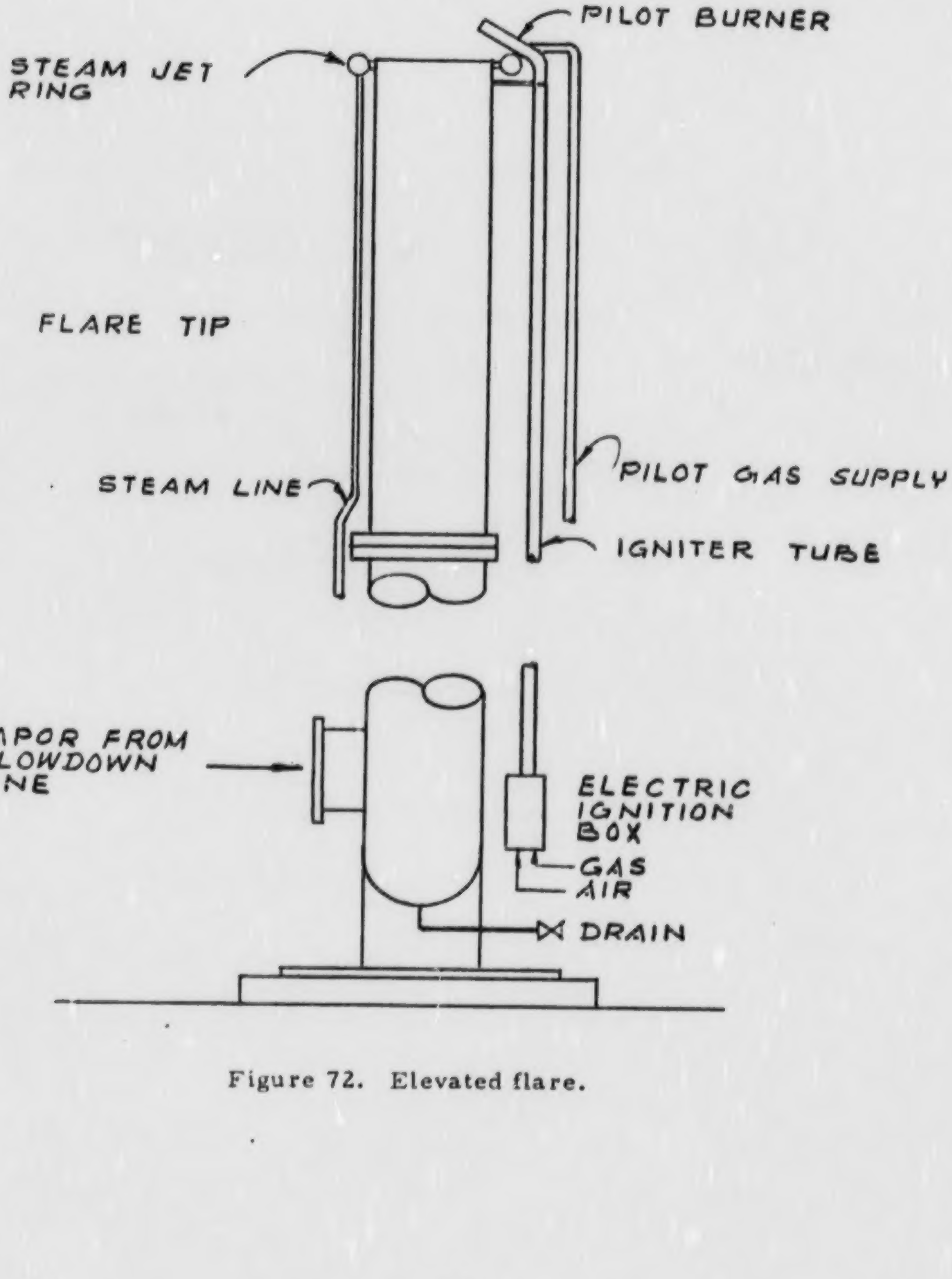

PILOT BURNER
STEAM JET RING
FLARE TIP
STEAM LINE
PILOT GAS SUPPLY
IGNITER TUBE
VAPOR FROM BLOWDOWN LINE
ELECTRIC IGNITION BOX
GAS
AIR
DRAIN

Figure 72. Elevated flare.

The flare consists of a vertical pipe extending to an elevation sufficiently higher than surrounding equipment and the ground so that the heat given off by the flame will not harm personnel or equipment. A pilot burner and ignition system is provided to insure that a flame is maintained during venting. The flare burner tip is equipped with a series of steam jets so placed that turbulence is produced in the flame, which leads to smokeless combustion. Smaller flares sometimes use air provided by a blower in place of the steam, but larger flares generally employ steam. To conserve steam, a control valve in the steam line is activated by a flow sensor in the flare line.

Another type of flare frequently encountered in refineries is the burning pit. They are generally reserved for very large gas flows during major emergencies and are connected to the blowdown system through a deep liquid seal that only opens when the elevated flare is overwhelmed. A simple burning pit may consist of a circular area enclosed by a wall, with inward-facing burners piercing the wall at intervals.

For additional information refer to "Air Pollution Engineering Manual" (Second Edition), John A. Danielsen, available from the Government Printing Office as EP4.9:40-2.

J. KNOCKOUT DRUMS

A knockout drum is a device for separating entrained liquid from a vapor stream. The separation is accomplished by increasing the area of the cross section available to the flowing stream, thus reducing the flow velocity and allowing the entrained liquid droplets to settle by gravity. In some knockout drums, the separation is improved by adding a mist eliminator in the upper section of the drum just ahead of the vapor outlet. The mist eliminator can take the form of a knitted wire pad that separates fine liquid droplets from the vapor by impingement. Figure 73 is a sketch of a typical vertical knockout drum. Horizontal knockout drums are also very commonly used. The level control shown on the figure is not a required feature and may be omitted where the volume of liquid to be separated is small.

K. SCRUBBERS

Scrubbers are devices for contacting a vapor with a liquid for the purpose of removing a contaminant from the vapor. For instance, a hydrocarbon gas stream containing H_2S can be scrubbed with a sodium hydroxide solution (caustic solution) to remove the H_2S. Another example would be the scrubbing of a gas stream with water to remove dust carried by the gas.

Figure 74 is a sketch of one of the many possible scrubber designs. In the sketch, ceramic saddle packing is used to promote intimate mixing of vapor and liquid. Other forms of packing and various types of trays can be used, or the vessel can be left empty with vapor-liquid contact being achieved by spraying the liquid into the vapor. The scrubber shown uses closed liquid circulation, implying that the liquid

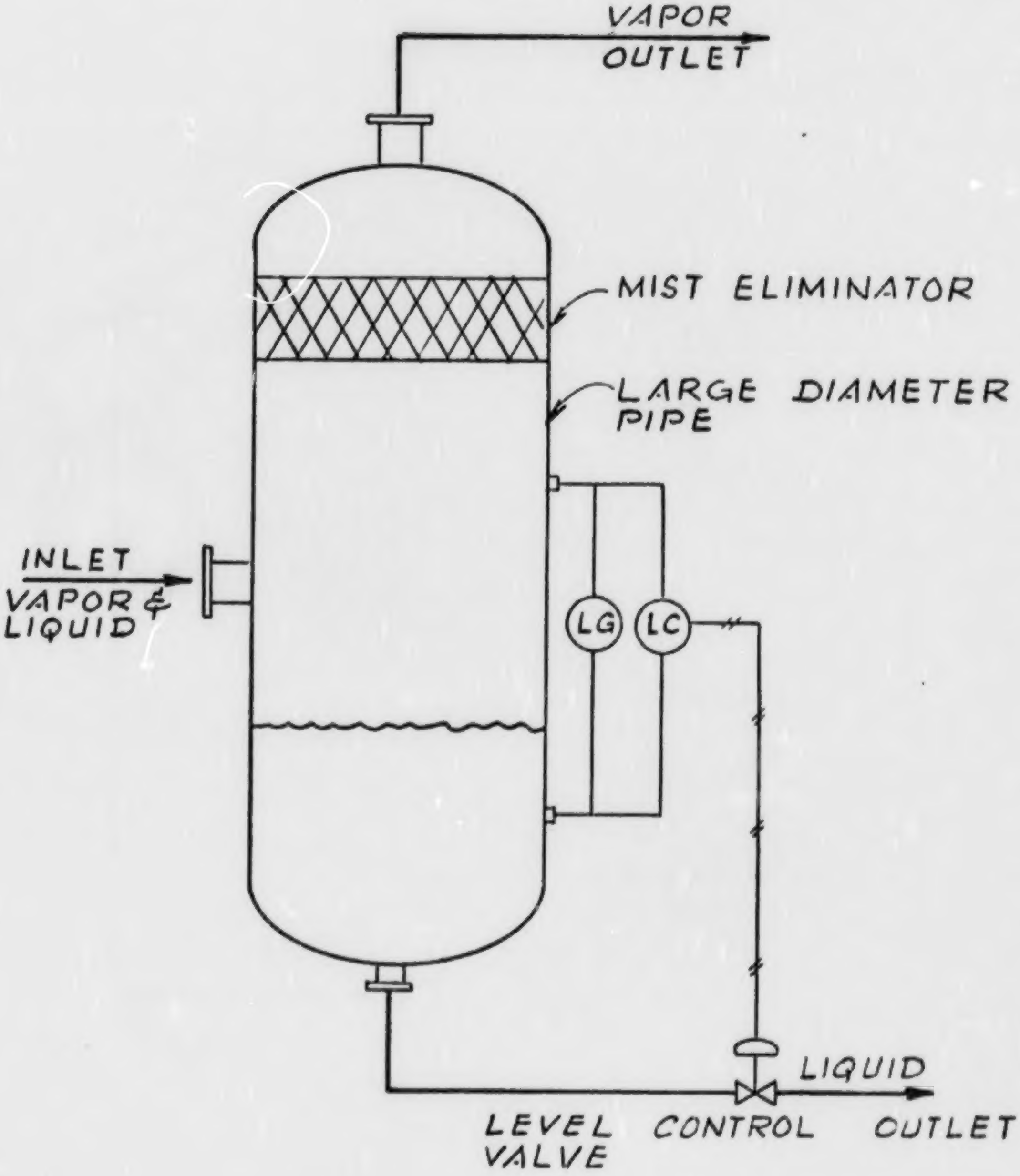

VAPOR OUTLET
MIST ELIMINATOR
LARGE DIAMETER PIPE
INLET VAPOR & LIQUID
LG
LC
LIQUID OUTLET
LEVEL CONTROL VALVE

Figure 73. Knockout drum.

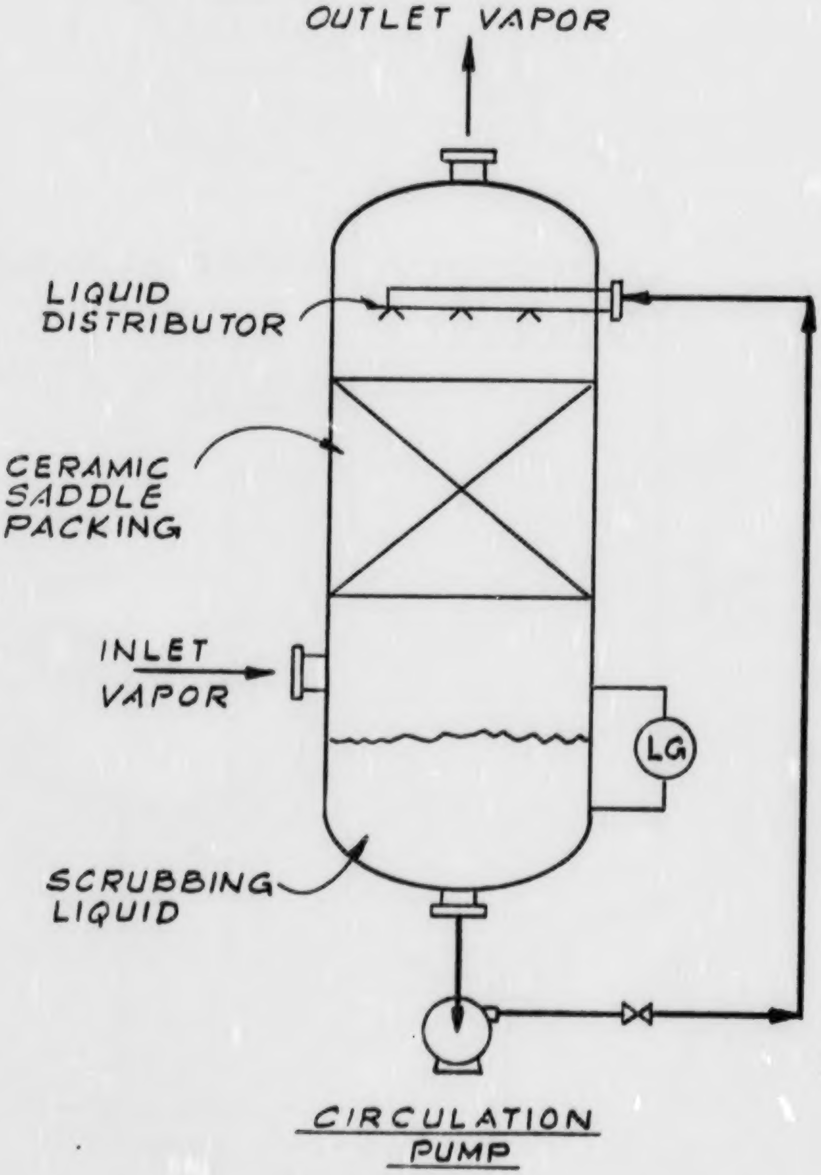

OUTLET VAPOR
LIQUID DISTRIBUTOR
CERAMIC SADDLE PACKING
INLET VAPOR
LG
SCRUBBING LIQUID
CIRCULATION PUMP

Figure 74. Scrubber.

will be replaced periodically. Other systems might employ once-through liquid circulation.

L. FRACTIONATORS

Fractionators are sometimes called fractionating towers, or distillation columns, or stills. They are liquid-vapor contacting devices that achieve a separation of feed components based on the difference in boiling points of the components. When a mixture of hydrocarbons is boiled the vapors produced are richer in the lighter, or lower-boiling-point components. If the vapors are condensed and the process repeated further enrichment of the lighter components will be obtained in the vapor. Similarly, if the liquid from the first step is boiled, the remaining liquid will contain a still higher concentration of heavy components. The fractionator shown in Figure 75 is a device to accomplish these steps in a continuous fashion.

Feed is introduced near the middle of the column onto the feed tray. Vapor rising from the tray below condenses in the liquid on the tray, vaporizing some of the liquid which travels up to the next tray. In this way, vapor originally formed by the reboiler at the bottom of the column supplies a vapor stream that passes up through the column, leaving as overhead vapor. The overhead vapor is condensed to liquid in the condenser. Part of this liquid is overhead, or light, product and the remainder is returned to the column as reflux to provide a source of liquid to the trays.

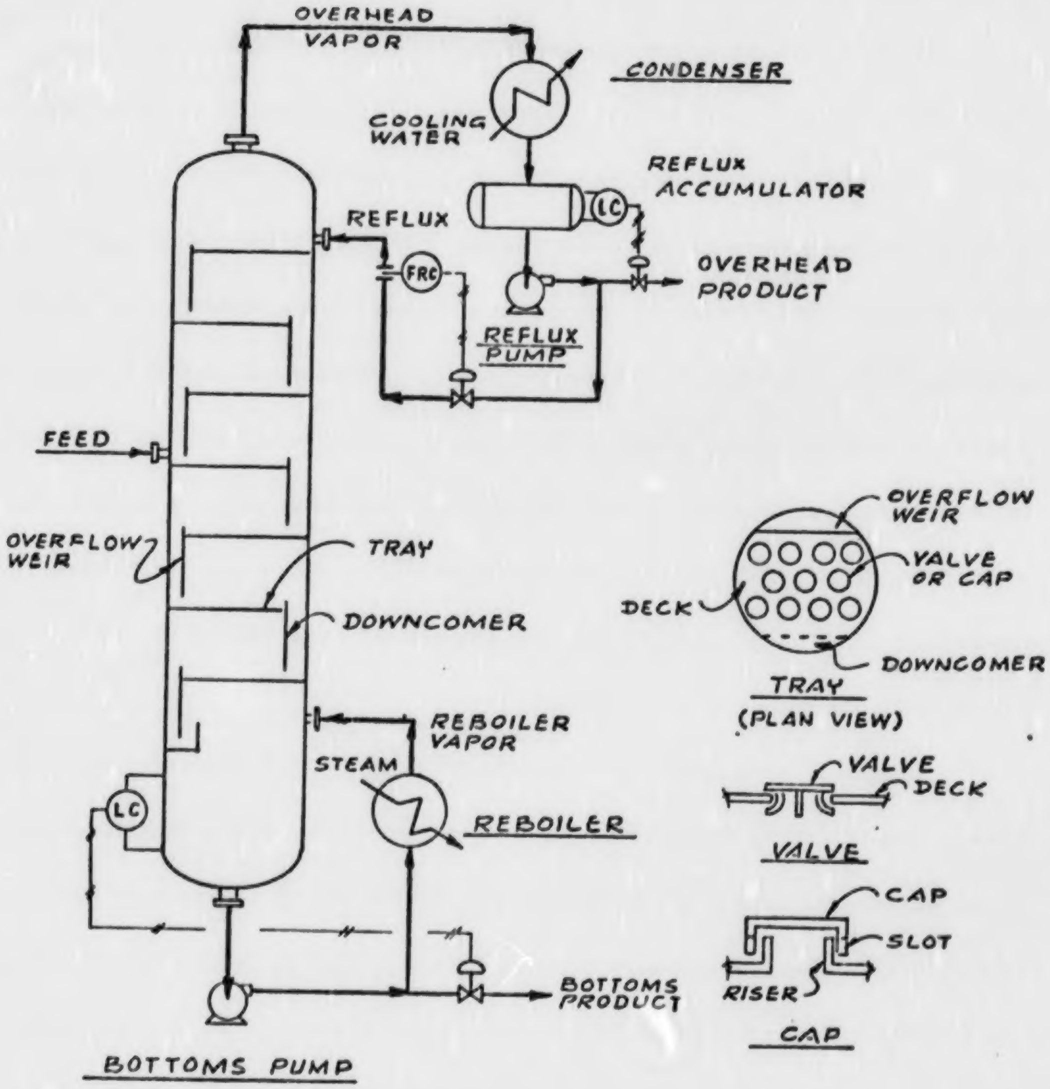

OVERHEAD VAPOR
CONDENSER
COOLING WATER
REFLUX ACCUMULATOR
LC
REFLUX
FRC
OVERHEAD PRODUCT
REFLUX PUMP
FEED
OVERFLOW WEIR
TRAY
DOWNCOMER
REBOILER VAPOR
STEAM
REBOILER
LC
BOTTOMS PRODUCT
BOTTOMS PUMP
OVERFLOW WEIR
VALVE OR CAP
DECK
DOWNCOMER
TRAY (PLAN VIEW)
VALVE
DECK
VALVE
CAP
SLOT
RISER
CAP

Figure 75. Fractionator.

The figure shows a fractionator that uses trays as vapor-liquid contacting devices. Details are shown for both valve trays and bubble cap trays, which are two of many types of trays. The combination of downcomer and overflow weir shown is used to maintain a liquid level on the tray and a vapor seal so that the vapor is forced to flow through the valves or caps. It is also possible to use shaped solids such as Raschig rings, Intalox saddles or Pall rings as contacting material. The column is filled with the rings or saddles and is called a packed column.

III. PROCESS INSTRUMENTATION

A. INTRODUCTION

Process instruments are widely used in refineries to indicate, record, and control the operating conditions and plant performance. Early processing plants contained only indicating instruments to assist the operator to control the plant operation manually. Modern refineries are highly automated with instruments which control process flows, temperatures, and pressures. Some refineries have computers which process operating data and recommend or execute changes in operating conditions.

B. IDENTIFICATION OF PROCESS INSTRUMENTS

Process instruments can be classified according to the variable being processed and its function. The variety of instrument types is best illustrated by the Instrument Society of America (ISA) code system. This code system is used on all flow sheets in this manual. A two or three-letter symbol is used for each instrument. A summary of the commonly used code letters is presented in Table 8. The symbol "FRC", for example, indicates an instrument which records and controls the flow rate. Other symbols are used to indicate whether the

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Table 8. INSTRUMENT IDENTIFICATION CODES*

Letter	Process (First Position)	Function (s) (Second and Third Position)
A	-	Alarm
C	Conductivity	Controller
D	Density	-
E	Electric variable	Element
F	Flow	-
G	-	Glass or gage
H	Hand or manual activation	-
I	-	Indicator
L	Level	Logging, scanning
M	Moisture	-
O	-	Orifice, restriction
pH	Acidity	-
P	Pressure	-
R	-	Recorder
S	Speed	Safety
T	Temperature	-
U	Unit	-
V	Viscosity	Valve
W	Weight	Well

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* Example: PSV = Pressure Safety Valve

instrument is board mounted in the control room or locally mounted within the plant.

A process instrumentation and control system consists of sensors that measure the process variable, transducers that convert the signal to electrical or mechanical form, gages, recording devices, transmitters that relay the signal to receiving instruments, control valves, and other instruments that affect the process stream behavior. Each of the major instrument categories is discussed below.

1. Indicators

An indicator shows the immediate condition of the process stream. It might be a thermometer gage, level glass, or manometer. In most refineries, operators take readings of various indicators in the plant at regular intervals. These data are generally recorded on operating sheets and filed for a limited time.

2. Recorders

A recorder takes an electric or pneumatic signal from a remote sensor and records it on a moving chart. Some recorders use circular charts that rotate as a pen traces the process signal. The normal time coverage of these charts is 24 hours. This type of recorder is widely used, but the current trend is to use strip charts which trace a process signal on a roll of paper as it moves from one roll to another. A strip-chart instrument will accumulate data from several days' operation on a single roll, which makes it easier to review and analyze the process operation over an extended period.

Care must be exercised in reading instrument charts. The charts are frequently graduated in units from one to ten or from one to one-hundred. The proper instrument value is obtained by multiplying the chart reading by a factor which is unique to that instrument system. These factors may be written on the instrument face or recorded in the instrument log book. The field engineer should check with the operating foreman to confirm that the correct factors are being used.

Care is also required in reading pulsating or cycling signals. An average of the high and low signals can be used to estimate the average value. The maximum reading can be used to estimate the instantaneous peak value.

3. Transmitters

Transmitters are devices used within the plant to relay signals from the measuring point to the receiving device. Transmitters are generally the electric or pneumatic type. The pneumatic transmitter in conjunction with force-balance measuring devices is in wide use today.

This system operates on a low-pressure instrument air system with signals transmitted through small-bore tubing.

4. Controllers

A controller is an instrument that receives a signal from the sensing element or transmitter, compares the signal to a predetermined value or set point, computes the action required to align the process variable, and executes the corrective action. Controllers operate on electrical, mechanical, hydraulic, and pneumatic signals. The pneumatic system is the most common type found in refineries.

5. Control Valves

The control valve is the final device in a control system. The valve opening is varied according to the pneumatic signal received. The valve position is adjusted through a diaphragm or bellows which responds to pressure changes. Control valves are discussed in more detail in Chapter II, Refinery Equipment.

C. FLOW MEASUREMENT

Flow metering devices fall into three categories: positive displacement, variable-area, and variable-head meters.

1. Positive Displacement Meters

The nutating piston or nutating disk meter is the most commonly used positive displacement meter. This meter is used primarily for liquids. The lobed rotor meter contains two lobed impellers and is used chiefly for high volume gas flow metering. Other types include the rotary vane meter (gases and liquids) and the liquid-sealed gas meters.

Velocity meters are based on the turbine principle. The velocity of the fluid actuates an impeller whose speed varies with flow rate. The turbine meter is the most frequently used type of velocity meter.

2. Variable-Area Meters

The piston meter and rotometer are based on the variable-flow area principle. A rotometer is a vertical tapered tube containing a float. The level of the float is determined by the balance between the weight of float and the force of the fluid passing between the float and the tube wall. The float level is read directly on a scale on the transparent tube.

The piston meter contains a piston which rises as the flow increases. As the piston rises additional orifice area is exposed. The level of the piston provides a direct indication of flow rate.

3. Variable-Head Meters

The most frequently encountered variable-head meters measure the pressure drop across a constriction in the line. An orifice plate or flow nozzle is often used to create the pressure loss. Streamlined restriction tubes, known as venturi tubes, are also used. A pitot tube measures the local fluid velocity in the line. A tube is placed in the flowing fluid facing upstream. The velocity pressure is converted to static-head reading. Pitot tubes can be used as portable instruments to measure gas flow rates from vents and ducts.

Weirs and flumes are used to measure flow rates in open channels. A weir is a dam with a notched opening. The height of the level in the notch indicates the flow rate. A flume is a narrow throat in the open channel. The level of the quiet fluid upstream of the flume indicates the flow rate.

D. TEMPERATURE MEASUREMENT

Temperature measurements in refineries are made with thermocouples, thermometers, and radiation pyrometers.

1. Thermocouples

Thermocouples are widely used in refineries to measure the temperature of process streams. When two dissimilar metals are connected in a circuit, an electric current will flow if a temperature difference exists between the two junctions. The thermocouple is placed in a protective tube or thermowell. Voltage signals from thermocouples are used to operate controllers, recorders, and multiple readout stations in control rooms.

2. Thermometers

The common liquid-in-glass thermometer is used as a temperature indicator in refineries. More common, however, is the bimetallic thermometer or temperature gauge. When two dissimilar metal strips are attached, a temperature change will cause unequal changes in length in the strips resulting in a deflection. Temperature gauges are placed in the plant to obtain local readings. Often only a thermowell is provided requiring the operator to insert a thermometer to obtain a reading.

3. Radiation Pyrometers

Radiation pyrometers are generally used where temperatures are extremely high or where other devices cannot be used in direct contact with the heat source. Radiation pyrometers measure the intensity of radiation from a hot source. A photocell or other detector converts the radiation to electrical current. Optical pyrometers compare the radiation intensity from the object in question to another hot source of known temperature such as a tungsten filament.

4. Resistance Thermometers

The resistance thermometer and filled-system thermometers are also used in refinery applications. The resistance thermometer is based on the change in electrical resistivity of metals with temperature. The element is placed in a protective tube similar to a thermowell. The filled-system thermometer measures the pressure change of an enclosed volume of gas or liquid.

E. PRESSURE MEASUREMENT

Pressure measuring instruments can be classified as elastic elements, gravity-balance manometers, and electrical pressure instruments.

1. Elastic Elements

Pressure indicating gauges commonly found throughout refineries operate on elastic elements, such as bellows, diaphragms, or bourdon tubes. When the elastic element is strained, a deflection indicates the pressure level. Sealing fluids are often used to protect the element from the process fluid.

2. Gravity-Balance Manometer

A U-tube or well filled with a liquid column will register a level differential under pressure. One side of the manometer is connected to the unknown pressure source and the other side is connected to atmosphere, vacuum, or other known pressure. A manometer can also be used to directly measure differential pressures on flow elements such as an orifice plate.

3. Electrical Pressure Instruments

The strain gauge operates on the principle of change in electric resistivity of a wire under strain or deformation. The strain gauge is used as a transducer to convert pressure signals to electric signals. High-vacuum pressures are also measured using electric or electronic principles. Resistance elements in a vacuum can be used to measure pressure indirectly by measuring gas thermal conductivity. The Knudsen gauge is a complex device for measuring vacuum pressures by measuring the deflection of molecules off heated vanes. Other types are based on the principle of gas ionization.

F. LEVEL MEASUREMENT

The measurement of liquid levels and liquid-liquid interface levels is widely practiced in refineries to control process operations. The simplest method of level measurement is direct observation. This can be done with a manually operated gauge tape or an externally mounted sight glass. Indirect methods of level determination are based on the location of an internal float, differences in physical properties of the two phases, or static head. Each of these is discussed briefly below:

1. Float Devices

The simple ball-float mechanism is widely used in refinery service to control liquid levels. A rod, attached to the ball float, is used to operate a level indicator, inlet valve, or pilot relay which, in turn, operates a pneumatic control system. In some cases, the float is located in a float cage connected to the vessel. Magnetic floats are also used to indicate levels.

2. Displacer Devices

The displacer type of liquid-level indicator has largely replaced the ball float. The displacer is a tube lighter than the liquid whose level is being measured. As the liquid level rises the displacer undergoes a buoyant force. This force is translated to torque in a rod or to pressure in a bellows located externally. The rod rotation or the bellows pressure is used to indicate level or transmit signals to a control system.

3. Hydrostatic Methods

Numerous hydrostatic methods are used to measure the static head of the liquid in a vessel. One method connects the liquid under static pressure to a diaphragm box. The diaphragm pressure is then metered to determine level. Mercury manometers and other differential pressure instruments are also used to measure static head.

G. ANALYTICAL INSTRUMENTS

A variety of special instruments is used to monitor product quality and control refinery operations. Some of these instruments are unique to the petroleum industry. Each refinery has a laboratory for quality control testing. In large refineries, the laboratory may contain sophisticated analytical equipment and perform limited research functions. In most refineries, the laboratory performs only routine tests.

These tests include determination of gravity, boiling point, flash point, viscosity, and sulfur and metals content. Gas chromatographs are occasionally used to analyze the composition of light hydrocarbon streams.

In most cases, refinery laboratory data can provide only clues to possible emission sources. Routine data on chemical and physical properties of process streams are useful in determining the normal plant operating charactistics. Deviation from normal operation indicates a possible plant upset which could result in temporary emission of pollutants.

H. COMPUTERS

Digital computers find widespread use in modern refineries and are often applied in process control. Shortly after computers became generally available, many people felt that within a few years entire refineries would be under the direct control of on-line computers. This did not come to pass, and at this time direct computer control is usually limited to sections of a processing unit or to a single piece of equipment. Computers are, however, very widely used to collect and display data and to provide information used in making process control decisions.

Where computers are used for on-line control, electric rather than pneumatic sensors and controllers are usually used. Signals from primary sensing elements are converted to low voltage electric signals that are in turn converted to binary codes acceptable to the computer. The computer is programmed to produce process control decisions which are converted from binary code to low voltage signals for transmission. The low voltage signal is used to control electric motors that position valves, etc.

IV. MONITORING INSTRUMENTATION

A. SOURCE MONITORING

1. Monitoring Systems

a. Approaches - Today source emissions are still measured manually. A sample is extracted from a point or series of points in a stack or duct and are analyzed in the laboratory or at some other remote site. The result of the analysis represents an integrated average of the emission parameter measured over the length of time the sample was collected.

While the field enforcement officer may request that such tests be made and may observe or even participate in the conduct of these tests, his principal concern will be in data that are immediately available and that can be correlated with physical observations made during an inspection or investigation. Greater use is now being made of newer measurement methods that permit immediate determination of some measurement variables related to emissions and that also can be used in the continuous monitoring mode.

Nader[1] has categorized these newer methods according to three criteria: (1) Is measurement made in situ (at the point of extraction) or on extracted sample; (2) Is a point measurement made or is the measurement integrated across a path; and (3) Is sensing on-site or remote? Since all extractive monitoring inherently involves point sampling, only in situ or remote sensing can involve the integrated sample mode. Table 9 lists those approaches that are at present in use or that seem feasible, considering the above criteria. Specific examples of these techniques will be given later.

Table 9. APPROACHES TO SOURCE MONITORING

Approach	Example
1. Extractive monitoring	Continuous analyzer on stack gas sample extracted from point or series of points in stack
2. In situ point monitoring	Sensor placed directly in stack at single point or series of points
3. Integrated in situ monitoring	Spectrometric or optical measurement made across stack
4. Integrated off-site monitoring	Remote sensing spectrometric or optical technique. May have active source or use solar energy

b. System Components - A source monitoring system consists of far more than the sensor or analysis device used. In the same reference, six component or component/operation combinations are given as parts of a source monitoring system. These are reproduced in Table 10.

A major problem may be encountered in satisfying the requirements of the site selection criteria as applied to source monitoring. In conventional extractive source testing where samples are removed for subsequent off-site analysis the New Source Performance Standards of the Environmental Protection Agency[2] call for a minimum of twelve sample traverse points in a stack if the sample location is eight stack or duct diameters downstream and two duct diameters upstream from any flow disturbance such as a bend, expansion, contraction or visible flame. If these location criteria cannot be met, additional traverse points are called for.

In the case of a continuous point source extractive monitor or an in situ point source monitoring device which is used in a permanent fixed installation, there will be only one sample point. This point should be relatable in terms of contaminant concentration to the true mean concentration established by traverse prior to the fixed installation. This relation cannot be expected to remain constant unless process and stack conditions (e.g., temperature and flow rate) continue to be the same as when the relation was originally established. Therefore, the field enforcement officer should determine, when observing such monitoring equipment, the precautions which have been taken to

Table 10. SYSTEM COMPONENTS AND OPERATIONS FOR STATIONARY SOURCE MONITORING

Component/Operation	Requirement
1. Sample site selection and execution	Representative sampling, consistent with intended interpretation of measurement
2. Sample transport (when applicable)	Transporting sample extract with minimum and/or known effects on sample integrity
3. Sample treatment (when applicable)	Physical and/or chemical conditioning of sample consistent with analytical operation with controlled and/or known effects on sample integrity
4. Sample analysis	Generation of qualitative and quantitative data on pollutant or parameter of interest
5. Data reduction and display	Calibrating and processing analog data and display of final data in format consistent with measurement objectives
6. Data interpretation	Relating the measurement data to the source environment within the limitations of the sampling and analytical operations

assure that the relation between the contaminant concentration as determined by the fixed monitor and the true concentration can be reasonably established. This problem is much less severe with an integrating or across the stack monitor, but still cannot be neglected.

A variety of other problems may be related to sample point or sample point environment. For example, in the case of an extractive monitor for sulfur dioxide in the tail gases from a sulfur recovery unit, any residual hydrogen sulfide may continue to react forming sulfur which may cause erroneous anazer readings or plug the sample line. The American Petroleum Institute[3] has suggested that the following environmental influences be considered when locating process or source monitoring analyzers: radian heat, mechanical shock and vibration, vulnerability to damage, electrical hazards, and weather. Further, analyzer installation points should have safe access for calibration, servicing and maintenance.

c. Monitoring Strategy - In addition to the sometimes severe environmental problems associated with source monitoring, e.g., high temperatures, excessive moisture, and presence of high contaminant concentrations, a major problem exists in obtaining representative test data. This is a result of the time variation in the process and distributional variation across stack or duct and fluctuations in contaminant loading.

The strategy approach in source monitoring should be to (1) examine the process and equipment for likelihood of these variations, (2) to pick a sampling point at which the variations will be at a minimum, and (3) to select a monitoring approach which, within available options, is best able to compensate for the variations.

One of the primary arguments in favor of source monitoring, of course, is the potential for obtaining a continuous record of contaminant concentrations, thus enabling a more accurate determination of the true emission rate. This is particularly true for gaseous contaminants. In the case of particulate extractive monitors where time variations are accompanied by flow rate changes, there should be an ability to vary the sampling rate to maintain isokinetic sampling conditions.

In the case of distributional variation, nonextractive across-the-stack integrating monitoring devices are much better able to minimize the effect of such variation.

2. Source Monitoring Interfaces

To present a source sample to a monitoring device in a form that will ensure a correct analysis and to ensure that the monitoring device will be able to function continuously and reliably, some accessory items are usually required. These are commonly classified as interfacing equipment. This equipment is designed (at least in the case of extractive monitors) to remove the sample from the stack; to transport it; to clean it; to alter temperature, water content, and possibly pressure; and to measure, and if necessary, to control its flow rate. The selection and design of this interfacing equipment in many cases is as important as the selection and design of the actual analytical device. It often costs as much or more to acquire and install the interfacing equipment as it does for the monitor itself. For example, in the case of an electrochemical type extractive monitor for sulfur dioxide, the purchase price of the analyzer is approximately $1, 100 and the total installation cost typically ranges from $6, 000 to $8, 000. In the case of an extractive photometric analyzer costing approximately $12, 000, with installation charges ranging from $6, 000 to $8, 000 the total installed cost can be $18, 000 to $20, 000. The important categories of interfacing equipment are discussed briefly below:

a. Probe and Materials of Construction - A probe is a device that is placed in the stack of an extractive monitor. Under clean, dry conditions, it may be a simple tube curved at the end to face the exhaust flow, or it may have an integral particulate filter as a preliminary clean-up device. These filters are usually of ceramic or sintered metal design to withstand temperature and to minimize adsorption effects for reactive gas sampling. Further, the probe may require heating to prevent moisture condensation or may incorporate internal static pressure taps to determine isokinetic sampling conditions in the case of particulate monitors.[4]

Materials of construction should be such as to reduce to a minimum wall losses through reaction, adsorption, or other depositions. Smooth, clean, nonreactive tubing such as borosilicate glass, Vycor, or stainless steel are preferred materials. If copper is used, it should be refrigeration grade. All probes and tubing should be cleaned thoroughly prior to installation. All valves, fittings, and seals should be compatible with the system and must be leak-proof.

b. Sample Conditioning - Sample conditioning is one of the major problems in source monitoring. This operation can include temperature reduction, moisture removal, particulate removal, and pressure reduction - all to be accomplished with a minimal or known effect on the component of interest.

Temperature reduction and moisture removal may both be done by cooling. In turn, the cooling may be accomplished directly by refrigeration or indirectly by dilution, although the latter step requires additional flow measurement and control. Unfortunately, the removal of moisture by cooling leaves a condensate which must be purged from the system. This is done by a trap - a device permitting discharge of water without loss of the gas sample. In the case of soluble gases such as sulfur dioxide, the moisture removal process by condensation will also result in the removal of some SO_2. Considerable effort has been expended by manufacturers of commercial equipment to alleviate this problem. One approach is to pass the gas through condensing systems as rapidly as possible with the trap located away from the main gas flow path. This reduces exposure of the gas stream to the condensate. Nevertheless, the probable loss of SO_2 should be evaluated, preferably by in-place sample spiking or by calibration.

Unwanted particulate matter which may clog lines or interfere with the measurement process is usually removed by filtration. Depending upon the loading and the operating schedule, a built-in inert gas back-flush system may be required to periodically remove accumulated particulate matter which increases back pressure and may cause increased sample losses. The filter media itself should be nonreactive, strong, resistant to moisture and corrosion, and nonadsorptive.

Recently, reverse permeation devices have been studied which will permit a gaseous contaminant of interest to pass from the sample stream through a semipermeable membrane barrier into a nonreactive carrier gas which then flows to the detector. The unwanted contaminating moisture and particulates are retained on the sample-gas side of the barrier. Because the permeation of the gas of interest is not quantitative but is a function of partial pressure (concentration) in the original stream, a careful calibration is required to translate the apparent analyzer concentration to the true concentration. These devices have not as yet been used extensively, but if successful could become an attractive solution to sample clean-up problems.

Pressure reduction may sometimes be necessary. If so, those making the installation should be cautious about effects of possible freezing, ice deposit, or hydrate formation. Figure 76 illustrates a typical sample system for an extractive monitoring device showing major interface components.

c. Sample Transport and Flow Measurement - In the case of extractive source monitors, a sample gas stream must be made to flow through the interfacing equipment to the actual sensor. This is accomplished by a vacuum-producing device, usually a pump, but sometimes an air or steam jet ejector. The latter require auxiliary services which are usually available in a refinery, but they are quite reliable and less subject to wear than are mechanical pumps.

In the case of concentration measuring sensors, flow rate does not directly affect results unless pressure limits are exceeded or unless pressure conditions inside the detector are changed from those at calibration. Where an indirect measure of mass is made, the sample flow rate enters directly into the

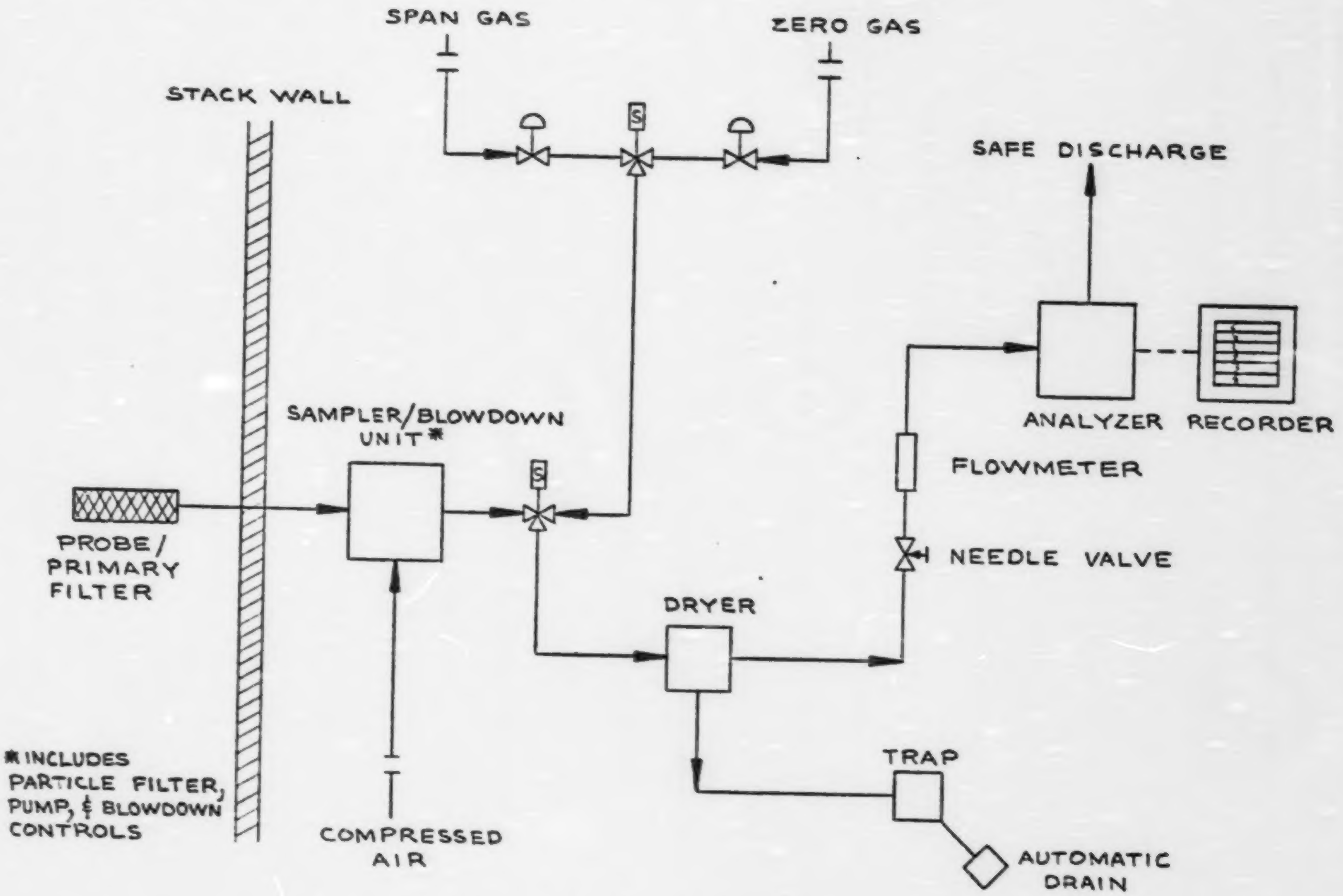
SPAN GAS
ZERO GAS
STACK WALL
S
S
SAFE DISCHARGE
SAMPLER/BLOWDOWN UNIT*
ANALYZER
RECORDER
FLOWMETER
PROBE/ PRIMARY FILTER
NEEDLE VALVE
DRYER
*INCLUDES PARTICLE FILTER, PUMP, & BLOWDOWN CONTROLS
TRAP
COMPRESSED AIR
AUTOMATIC DRAIN

Figure 76. Typical stack monitoring system.

final calculation of emission rate. In any case, flow should be at a rate to minimize wall losses and to avoid unusually long response times which are not consistent with possible rate-of-concentration variation.

Sample flow rates may be measured by a variety of measuring devices including calibrated nozzles and orifices and rotameters. The latter are probably the most commonly used. They are indirectly sensitive to temperature by its effect on carrier gas viscosity and are subject to wear of float and tube which also affects calibration. They should be used with care.

As earlier mentioned, isokinetic flow conditions must be maintained when sampling particulates where particle diameter-exceeds about 3 μm. If sampling velocity in the probe is higher than that in the stack, a disproportionate number of smaller particles will be present in the sample. If probe velocity is lower than stack velocity, a higher proportion of larger particles will be present in the sample stream. It may be desirable to have a sample flow rate controller which is actuated by a stack flow rate sensing device.

If mass emission rates are to be obtained, total exhaust flow must be measured regardless of whether extractive or nonextractive monitoring equipment is used. Although pitot tubes may be used as in conventional batch source testing,[4] an instrumental approach using a transducer which produces an electrical signal may be useful for permanent installations or those used to control sample flow rate. Recently, a heated thermopile velocity sensor has been marketed in which fluidic control of an inert gas flow over the thermopile is utilized instead of the stack gas itself. This permits operation in contaminated conditions without the necessity of cleaning the gas stream to be measured.

3. Calibration

Calibration requires relating the readout of the source monitor to the true concentration of the contaminant in the source being measured. A full-scale calibration involving the in-place introduction of a known concentration of the contaminant to the analyzer under stack conditions would be desirable, but to date, this has been difficult to do on a practical basis. A suggested approach is to inject a sample "slug" near the inlet to the probe.[1] This might be done by using a probe with a sample loop isolated by valves such as is done sometimes in introducing samples to a gas chromatograph. If in-place calibration is not practical, the sensor should be removed periodically for calibration.

A problem exists with integrated in situ monitoring devices such as open path correlation spectrophotometers and light transmittance devices. Any calibration performed outside the stack will suffer from the problem of duplicating alignment of source and sensor when installed. When using monitors for specific compounds, a regular schedule of referee analyses should be performed. For light-transmitting devices, the zero transmittance point can be obtained by blocking the light path, but a true 100% transmittance can only be obtained during shutdown conditions.

4. Source Monitoring Instruments

In recent years, many firms have been working on the development of continuous source monitoring instruments. Relatively few of the devices have reached full commercial status. The field enforcement officer should be generally familiar with the types of continuous monitoring systems in use or soon to be available. The principal types for the major air pollutants and their principal points of application are described here.

a. Gaseous contaminants

(1) Sulfur dioxide - The potential for sulfur dioxide emission exists in any combustion operation in which sulfur-containing fuel is burned - sulfur recovery plants, catalyst regeneration and other decoking operations, and some treating units.

Most source monitors available for sulfur dioxide determination are based upon the extractive monitoring concept. The two having the widest application involve the nondispersive infrared (NDIR) principle and an electrochemical approach. The nondispersive infrared technique involves the absorption of infrared energy by sample gas in a cell. Instead of using dispersive optical elements to obtain specificity, the infrared absorbing properties of the gas of interest are used. This is done by using the gas of interest either in a sensitizing cell or in a detector cell. In the first case, a differential thermopile is used for detection and, in the second, a capacitor microphone is used. The thermopile type is less sensitive but is also less sensitive to vibration and shock. In any case, the NDIR method is quite specific. It requires moisture and particulate removal to keep optical surfaces clean. The measurement is not highly sensitive to flow rate, but cell pressure must be maintained at the same level as during calibration.

The electrochemical sensor operates by producing an electric signal through electrooxidation of sulfur dioxide. In this particular class of electrometric instruments, the bulk gas flow does not pass through an electrolyte, but rather the gas of interest passes through a semipermeable membrane to the cell. As in the case of the nondispersive infrared analyzer, the instrument is not directly sensitive to flow rate but must be operated at constant pressure. Moisture and particulates must be removed and temperature is normally limited to 110° F.

Water removal systems for all sulfur dioxide monitors should be designed so as to minimize contact time between the gas stream and condensate to reduce the possibility of sulfur dioxide adsorption. The dilution approach to cooling and humidity reduction might be particularly attractive in sulfur dioxide analysis systems.

At least one commercial in situ sulfur dioxide analyzer is available. It is based upon the principle of ultraviolet correlation spectrometry. Although it is a dispersive technique, specificity is obtained by comparing the spectrum obtained with a correlation mask instead of selecting a particular wavelength interval as representative of the compound of interest. Physically, a tubular slotted probe is inserted in the stack so that flue gas continuously passes through the slot. Ultraviolet light shines through the flowing sample and is reflected by a mirror at the end of the slot back to the spectrometer head. An electrical signal proportional to the sulfur dioxide concentration results which is processed and displayed. Compensation for particulate accumulation on the optics is provided by automatic adjustment of the gain on the photomultiplier in the detector to reflect overall light intensity. Obviously, this accumulation cannot be permitted to continue indefinitely. Very little practical experience is available with this analyzer.

(2) Carbon monoxide - The principal source of carbon monoxide emissions from refinery operations is the regenerator of a fluid catalytic cracking unit. Carbon on the catalyst is burned off with less than the stoichiometric quantity of air. This results in appreciable carbon monoxide formation instead of total conversion of the carbon to carbon dioxide. In most cases there will be an afterburner, commonly called a "CO

boiler" in which the carbon monoxide is burned. While there are other possible sources such as other types of decokers, fluid cokers, engines, and incinerators, the most likely point of application for carbon monoxide monitoring is in connection with the fluid catalytic cracking regenerator.

The most frequently used technique for carbon monoxide monitoring is the extractive nondispersive infrared method. Fundamentally, the same type of sample conditioning equipment and analyzer is used as previously described for sulfur dioxide. The sensitizing cell would, of course, be filled with a carbon monoxide mixture instead of sulfur dioxide.

Electrochemical sensors used in conjunction with extractive monitoring techniques are also available, but there is much less experience with this method available to date.

It is entirely possible that in situ open path infrared spectrophotometric procedures will come into use, but they are still in the research and prototype stages.

(3) Nitrogen oxides - In refineries, almost all emissions of nitrogen oxides are from combustion processes and are predominantly in the form of nitric oxide (NO). Therefore, heaters, boilers, catalyst regenerators, furnaces, engines, flares, and other miscellaneous combustion processes may be considered as potential candidates for monitoring. It is likely, though, that only the larger sources, even in the future, will have monitoring

equipment installed.

There are many techniques for monitoring nitrogen oxides. These include both extractive, in situ, and remote sensing. These techniques are for the most part specific for either nitric oxide or nitrogen dioxide. Thus in the case of the extractive monitoring approach, where this is the case, conversion of NO to NO_2 to NO may have to be employed. Obviously this is not practicable in the case of in situ open-path or remote sensing techniques.

The extractive monitoring techniques available include:

- Electrochemical sensors - Fundamentally, these use the same general principle as similar devices for sulfur dioxide and carbon monoxide. The semipermeable membrane and electrolyte are optimized to give the necessary specificity. The commercially available sensors respond to both nitric oxide and nitrogen dioxide, although the relative response to nitric oxide is usually greater. Where the ratio of nitric oxide to nitrogen dioxide is known and constant, this is not a serious deficiency.

- Chemiluminescence - These analyzers operate on the principle of light emission resulting from the reaction between nitric oxide and ozone. The analyzer incorporates a built-in ozonizer which provides a stream of ozonized air to react with the sample stream. If nitrogen dioxide is to be determined, the sample stream must first pass through a catalytic decomposition section. Both particulate contamination and water must be removed. Special care must be taken or operation must be at reduced pressure if SO_2 or CO_2 are present in significant quantities, as both compounds act to quench the chemiluminescent reaction. Several manufacturers offer commercial instruments. All must be operated, calibrated, and serviced with considerable care.

- Ultraviolet-visible spectrometry - At least one manufacturer offers a split-beam filter photometer of this type for analysis of NO_2. If NO is to be determined, it must first be oxidized to NO_2. One approach used is to oxidize the NO with O_2 at approximately five atmospheres pressure. As is the case with most extractive gas monitors, particulates and water must be removed. Calibration is usually accomplished with a standard optical filter, but the zeroing operation uses a zero gas supply.

In situ open path or remote sensing is possible for nitrogen dioxide with the use of ultraviolet correlation spectrometry. The same general approach is used as when the technique is applied for sulfur dioxide. Because nitric oxide is not detected, the application is limited.

(4) Hydrocarbons - The major potential hydrocarbon losses in a refinery are from storage and product transfer. In most cases, source monitoring is not applicable. There are many other smaller sources such as blow down systems, vacuum jets, barometric condensers, air blowers, emergency vents, and fume incinerators where monitoring conceivably could be applied. So far, little effort has been made in this direction.

Three extractive monitoring techniques are applicable to hydrocarbons. One is the nondispersive infrared method previously discussed. The second is hydrogen flame ionization detection in which the presence of hydrocarbons in a sample stream flowing through a hydrogen flame increases the ionflow between two electrodes thus producing a signal proportional to the hydrocarbon concentration. The selective combustion analyzer technique is a third. Particulates and most water should be removed from the sample although the flame ionization method is not so sensitive to the presence of water as the other techniques.

(5) Miscellaneous gaseous contaminants - Hydrogen sulfide, mercaptans, ammonia, phenols, and other organic compounds may be discharged from catalyst regenerators, treating units,

air blowers, hydrogen sulfide recovery systems, and fume incinerators. One of the techniques previously mentioned for other contaminants can also be applied to most of these compounds. Monitoring for hydrogen sulfide is a more common practice than is monitoring for the contaminants of lesser importance. Again, most of the techniques applicable would be based upon extractive monitoring.

b. Particulates - The term particulates, here, covers smoke, dusts and fumes, and liquid phase aerosols. It is obvious that a great variety of sizes, particles, densities, shapes, optical properties, rigidity, and surface characteristics may be covered by this definition. In a refinery, we shall mainly be concerned with smoke, catalyst dust, coke breeze, and liquid aerosols. Because of the high reliability of combustion control now available, the major particulate problem from refineries is catalyst fines lost from fluid catalytic cracking unit regenerators.

(1) Optical - A variety of devices may be included in this category such as single-particle, light-scattering instruments, nephelometers, and opacity meters. The latter is the one in current use for source monitoring and includes the long available smoke meters. Using the earlier mentioned classification system, opacity instruments would be listed under the in situ open path class.

In recent times, considerable effort has been devoted to the adaptation of opacity instruments so as to enable the determination of mass concentration from light transmittance readings. Ensor and Pilat[5] have recently described in some detail the theory and assumptions necessary to make such calculations. In their expression, mass concentration is a function of particle density, optical path length, optical density $\left(\ln \frac{I}{I_o}\right)$, and a "K" factor. In turn, this "K" factor is a constant which is dependent upon particle diameter, wavelength of source light, refractive index of the particle, size frequency distribution, and scattering efficiency based upon particle shape. It is quite obvious that the "K" developed for any given particulate emission is quite unique. Any change in the several parameters listed above can affect the validity of the relation between light transmittance and mass concentration.

A number of installation and operational problems affect the reliability of opacity measurements in addition to those related to fundamental design. In large part, these are related to source and receiver alignment, cleaning of optical surfaces exposed to the stack gases, and to problems of calibration and zeroing. A variety of techniques has been used to facilitate maintaining cleanliness of optical surfaces. They include using recessed mounts with partial isolation of surfaces by purge air to cleaning technique based upon air blast and water jets. Even with the best of these, some manual cleaning is necessary at varying intervals.

Both infrared and visible light sources are used for instruments now available commercially. While most systems have the transmitted light sensing unit mounted opposite the light source, at least one now offers a dual beam unit with a corner cube reflector making possible the mounting of the source and receiver in the same housing.

It is important that the field enforcement officer understand the exact nature of any opacity device used for mass-loading determination, its limitations, and its operating requirements.

(2) Particle mass sensors - At least two devices are now available which are stated to be direct mass sensing devices. Both are in fairly early stages of development as far as source monitoring applications are concerned. The first described uses the principle of beta radiation attenuation. In this approach, an extractive sampling system dilutes and moves a sample stream of stack gas to a sequential filter tape mechanism where an integrated filter sample is obtained over some pre-set time period. Following this, the tape is advanced so as to be exposed to a beta radiation source. On the other side of the tape a sensing device measures the attenuation of the beta radiation. This attenuation has been found to be almost directly proportional

to the mass between the source and detector. The procedure does not give a truly continuous measurement but rather a series of integrated values over finite time periods. As is the case with an extractive sampling procedure for particulates, provision should be made for isokinetic sampling. Also care must be taken to maintain the integrity of the sample. Systems presently available have three major components as follows: (1) sampling probe and diluter, (2) collector unit containing pump, filter tape system, and beta radiation gage, and (3) control and readout units in which computation of mass concentration is made from mass and flow data. The collector unit should be near the source while the control and readout unit may be located remotely.

Another type of mass sensor involves the use of the piezoelectric principle. Here particles in a sample stream are deposited by electrical precipitation on a piezoelectric quartz crystal oscillating at its resonant frequency. Since the resonant frequency is mass dependent, the rate of change of this frequency can be measured by an appropriate detector circuit and related to the increase of mass on the crystal caused by the particulate deposit. At higher concentrations, dilution may be required. Also the effective particle size range of one instrument is stated to be limited to .01 to 20 μm. Among the operational problems that have to be considered are the requirement for periodic cleaning of the crystal and ensuring that liquid water is not deposited and cause spurious readings.

(3) Electrical - One type of particulate monitoring device is an extractive monitor which utilizes the charge transfer principle. In this instrument, particles in the sampled gas stream pass by a sensor without being collected but result in an electrical disturbance changing the current flow in the detector with a logarithmic dependence upon particle mass flow. Relatively little experience is available with this type of analyzer. Calibration is obviously a problem as is sample handling.

(4) Costs - A brief word is in order about present day costs of source monitoring instruments and installations keeping in mind that such figures may become dated rapidly. One of the lower cost sensors is the electrochemical sensor. For the sensor only, costs for a single parameter instrument are in the range of $1,000 to $1,500. Total installed cost including site work, sample handling system, and recorder may easily reach $6,000 to $8,000. At the higher end of the range, a completely installed spectrophotometric system may reach $18,000 to $20,000, based upon an analyzer cost of $14,000. The installed cost of one of the more expensive opacity instruments, including purge air systems, isolation shutters, and other accessories can reach $6,000 to $7,000. Other types of particle monitoring devices including the mass sensors may have installed costs

ranging up to $20,000. It seems obvious that even for a large company the installation of continuous monitoring devices cannot be considered a trivial expense, particularly when the continuing costs for servicing, calibration, repair and data processing are considered.

B. PERIMETER MONITORING

Contaminant monitoring as applied to the field surveillance of petroleum refineries can be more broadly interpreted than direct source monitoring alone. For one thing, not all sources of air contaminants are easily subject to direct source testing or monitoring. Such sources would include pump seals, valves, fittings, storage tanks, barometric condensers, oil water separators, pressure relief systems, most emergency flares, and other relatively minor sources. Further, it will be some time in the future before even most potentially major sources will be equipped with fully effective direct source monitoring instruments. To fill these gaps, the concept of perimeter or source oriented ambient air monitoring may be applied.

Source, meteorological, and receptor oriented criteria are all important in designing and establishing a perimeter air monitoring effort. The source oriented information would include an emission inventory for normal operation including points of emission and detailed information on potential major point sources of emission including stack location, stack height and maximum expected emission rate in the event of control equipment failure.

The meteorological data required involves wind speed and direction and atmospheric stability. If available, a wind rose and stability wind rose are most useful. A wind rose gives the frequency of occurrence for each wind direction (usually 16 points) and wind speed class (nine classes in standard Weather Bureau use) for the period under consideration. A stability wind rose gives the same type of information for each stability class. For maximum utility both seasonal and annual wind roses should be obtained.

The source and climatological data thus developed may be applied through the use of a diffusion model to predict points of maximum expected concentration and concentration isopleths for various averaging times and seasons. Turner[6] has prepared a workbook on the practical application of these models while Stern[7] has reported on the current status of a variety of modelling techniques.

Receptor and effects oriented information are also useful in planning a perimeter monitoring procedure. Should significant information be available relating to locations of odor complaints and materials or vegetation damage that clearly is related to past refinery operations, it should be used to modify or support monitoring planning based upon emission and meteorological data.

1. Continuous Monitoring

This approach involves the use of automatic, continuous, recording air sampling instruments. Such instruments are normally located in specially prepared fixed sampling sites or in mobile equipment. A significant investment is usually required and special precautions are necessary to ensure proper calibration, operation, and maintenance. Descriptions of such monitoring networks have been prepared by Bryan[8] and the Office of Air Programs of the Environmental Protection Agency[9].

Both fixed and mobile sites have advantages. In some cases the criterion will be availability of land or shelter where the optimum site locations have been determined through diffusion modelling process. Because the modelling process can only approximate expected conditions, the additional flexibility of a mobile station may be advantageous. On the other hand, a mobile station is generally more costly than equipping a permanent site and can require more manpower. It is particularly important in the case of perimeter or source oriented ambient monitoring systems to obtain wind speed and direction data concurrently with the contaminant data.

As a general principle, perimeter monitoring is most effective at points reasonably close to the probable source of expected contaminants. As distances increase, the contribution from a single source to the total ambient air loading of a given contaminant is reduced and a point will be reached where this contribution is nearly indistinguishable by ordinary monitoring means. Obviously, the contribution from a large point source in a remote area having no other point or area sources could be distinguished at greater distances than could the same source in the midst of similar sources.

At the other extreme, contaminants discharged from elevated point sources will not reach the surface of the ground closer than some finite distance from the source. Even under unstable plume looping conditions this distance may be several stack heights. Even though these latter conditions give rise to high concentrations at point of impact, the values can be expected to fluctuate rapidly due to vertical and lateral plume eddying movements. Thus some compromise must be reached in station siting so as to satisfy two conditions: (1) the sites must be close enough so that the contribution from the source involved can be clearly distinguished, and (2) the sampling or monitoring network must be dense enough at the given distance from the source that the emissions will be detected.

2. Integrated or Static Monitoring

Integrated monitoring systems may be either active or passive. That is they may involve the active sampling of air by means of a powered device moving air through or over a collection or sampling device, such as a bubbler train or a filter, or they may involve use of effects packages which are merely exposed to the normal free passage of ambient air. This latter group would include sticky paper, greased glass slides, sulfation plates, fabrics, metal plates, etc. In general, a much denser network of intermittent or static sampling sites is practical as compared to continuous monitoring. This results from the lower cost, lesser demands for space and power, and lower level of manpower skills required.

The resolution of data obtained from intermittent or static monitoring equipment takes longer than that from continuous monitoring so it is less suitable for episodic sampling. On the other hand, in preplanned situations such as might be the case with the application of an intermittent control strategy sufficient notice should be available to make the use of intermittent air sampling devices practicable and useful.

C. PORTABLE SAMPLING EQUIPMENT

The field enforcement officer may find it advantageous to use special portable sampling and analysis equipment during some phases of refinery inspection or in the investigation of complaints. For one thing not all potential sources of air pollution in refineries are well-defined stacks serving a major process or operation. Such miscellaneous sources would include leaks from pumps, fittings, and relief valves either into air or into cooling water later passed through cooling towers; oil-water separators; sumps; wastewater handling and storage; low-level minor process vents; storage tanks; low-level flares and spillage.

In many of these sources, general housekeeping and maintenance is closely related to the degree of contaminant loss. Further, the character of contaminants likely to be lost from these miscellaneous sources includes many of those of significant nuisance potential because of odor. These include hydrogen sulfide, mercaptans, aromatic hydrocarbons, amines, and other nitrogen bases to mention but a few.

1. Use of Portable Sampling Equipment

The field enforcement officer should be very careful in the use and interpretation of data collected by portable equipment. First of all, by very nature of the sources involved, many of these losses may be concentrated but very small in volumetric or mass flow. The actual ambient concentration, particularly near the source, will be highly variable and greatly affected by atmospheric or meteorological conditions. Thus the inspector should record over a period of time the values of a particular measurement made in any given area of the refinery or close proximity to establish a range of normal or expected values. In some cases, it will be more satisfactory to collect an integrated sample using nonreactive flexible bags or miniaturized integrated sampling devices, such as impingers, to obtain a more representative value. Of course, if one is leak tracing, a fast response system is desirable.

The field enforcement officer may also use portable sampling equipment during investigation of complaints. This equipment is operated at the point of the complaints or in a systematic perimeter check of the suspected source. Some knowledge of wind speed and direction and atmospheric stability will be needed to interpret such data.

2. Types of Portable Sampling Equipment

A variety of sampling and analysis equipment is available ranging from manually operated devices to portable, continuous, direct-reading analyzers.

One of the commonest portable devices is that based upon the use of indicator tubes. These tubes are sealed ampules containing a reagent on a solid substrate which are inserted into an air sampling device immediately following the breaking of the two sealed ends. A known amount of air is drawn through the tube by a squeeze bulb, hand pump, or a battery-driven air pump. Following exposure, the tube is compared against a standard by use of a length of stain measurement or degree of coloration to determine the concentration of the contaminant in the air sampled. A great variety of indicator tubes is available, some of which have been tested by the Bureau of Mines or other groups concerned with occupational health. The accuracy and sensitivity are, of course, generally poorer than instrumental methods of analysis. In some situations, it may be the only practicable approach.

As earlier mentioned, the field operation may be limited to sampling only with analyses to be performed in the laboratory. Commonly this approach involves the use of sampling bags, liquid impingers, filters, and perhaps precipitators or impactor devices. This type of collection should be performed as directed by a competent chemist or other air sampling specialist.

Finally, there are a substantial number of portable continuous analyzers. Generally, they are equipped with a direct-reading meter and only occasionally used with a miniature recorder. Perhaps the most common such instrument is the combustible gas analyzer. In this instrument an air sample is drawn over a heated element connected in an electric bridge circuit. Any combustibles present are oxidized over the surface of the element causing a temperature rise and consequent change in resistance of the element. By appropriate circuitry this resistance change causes a meter displacement proportional to concentration. However, the concentration shown is only relative and the instrument must be calibrated in terms of the material of interest. Other combustible gases or vapors will cause a response but the concentration indicated will not be correct.

Combustible gas analyzers have also been long available for carbon monoxide. In this analyzer, the resistance element is in a special catalyst and held at a temperature so that only carbon monoxide will be oxidized and thus cause a response. There can be some interference from large concentrations of the more easily oxidized hydrocarbons, such as ethylene.

Portable sampling instruments are available for hydrogen sulfide and sulfur dioxide. One for sulfur dioxide is based upon the conductivity principle and uses a plunger pump to draw the sample. Other instruments for hydrogen sulfide use the bromocoulometric or titrimetric approach.

In recent years there has been considerable development of the electrochemical cell type of instrument which is essentially the same in principle as those used for fixed source or ambient air monitoring. Analyzers based upon this principle are available for H_2S, NO_2, NO, Cl_2, HCN, $COCl_2$, SO_2, and CO. Specificity is obtained by the use of selective prefilters, semipermeable membranes, electrolyte material, electronic circuitry, or a combination of one or more of these approaches.

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V. MAINTENANCE OF REFINERY RECORDS FOR USE BY AIR POLLUTION CONTROL FIELD ENFORCEMENT OFFICERS

A. INTRODUCTION

1. Necessity of Keeping Records

The recording and filing of operational data is a requisite for efficient and economical plant operation in refineries and most other industries. Much of this information is related to throughput, turnarounds, upsets, emergency venting, maintenance, source monitoring, and ambient air monitoring and is, therefore, valuable in the effective enforcement of air pollution control rules and regulations. Field enforcement personnel, in addition to making observations for violations of visible emission standards, perform other duties which, in part, depend upon information from refinery records. These other duties include:

- Emissions Inventories - cataloging point sources according to type and quantity of air contaminants emitted;
- Source Registration Monitoring - determining that all sources covered by the agency's regulations have been duly registered with the agency;

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- Permit Compliance Investigations - checking to ensure that permits have been granted for all applicable processes and equipment and their modifications.
- Complaint Investigation - determining cause of complaint, recording pertinent data, issuing violation notices if appropriate, and ascertaining adequacy of plans for prevention of future incidents;
- Episode Management - periodically reviewing emergency procedure plans; checking that all shutdown procedures are being implemented during periods of process curtailment; coordinating with other agencies participating in pollution reduction effort;
- Compliance Plan Status Inspection - checking to see that engineering, procurement, installation, and testing of equipment is proceeding according to the approved plan.
- Source Compliance Monitoring - determining that all sources are in compliance with applicable emission standards (particularly important where the agency does not have a permit system).

2. Availability of Records to the Inspector

To conserve time and effort, data files should be kept in a specified location preferably where the enforcement officer meets the individual designated to accompany him on inspections. Refinery management personnel must also be aware of the location and content of these files so that in the event the primary contact is not available, an alternate can be assigned. Files kept at the home office, if not on the refinery premises, are of little immediate value. The unavailability of data may result in time delays that reduce the field enforcement officer's effectiveness and waste the time of plant personnel.

3. How Records will be Used

Data contained in these records will have four primary uses.

a. Permit and Source Registration Identification - Flow charts, engineering drawings, and equipment description will be used to designate the exact location, capacity and configuration of a system or permit unit.[1] This descriptive information is necessary to preclude modifications without agency concurrence, to estimate increases of emissions due to process or feed changes, and to determine the location of monitoring systems (see Chapter IV).

b. Emissions Inventories - Data usable for estimating emissions are contained in special reports such as sulfur balances in fuel gases (Figure 77) and estimates of losses from pumps, valves, emergency flaring, tanks, and transfer processes. Additional direct data can be found in logged values from source monitors, air monitoring devices, plant operations reports, analyzers, sulfur and hydrocarbon balance forms, and odor surveys.

REFINERY DAILY FUEL USE REPORT

Company Name______________________________________

Address______________________________________Zip____________Tel. No._______________

Day of Month	Gas Curtailed	Fuel Use Data						
		Fuel Oil Barrels	Weight % Sulfur	Gravity API	Natural Gas MCF	Refinery Gas MCF	SO_2 Refinery Gas, Tons	Remarks
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								
31								
Total								

Signature of Company Representative____________________________Title______________________

Figure 77. Fuel use/sulfur balance report

c. Emergency Action - Plans and procedures for emergency action are among the documents which will be duplicated in the enforcement agency's files. These records will serve as a checklist for the field enforcement officer during periods of curtailment of operations and during dry runs to simulate emergency operations. These plans must be updated periodically to account for process changes, procedural modifications, and errors detected during practice runs.

d. Legal Action - Incident and complaint investigations, court actions, and variance board activity will require data from all of the records described above. For example, the point of emission of excessive odors may be traced from an incident described in an operator's log or from an inplant odor survey record (Figure 78).

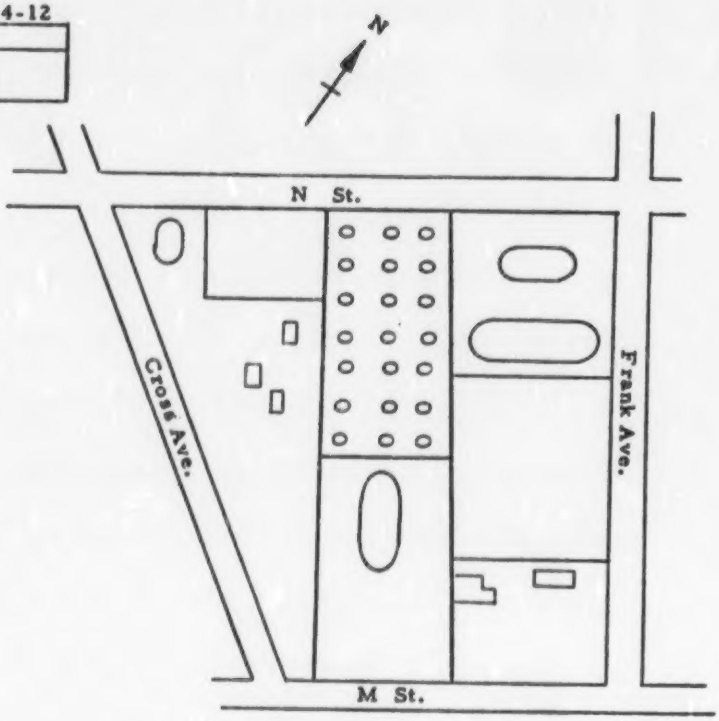
Some of the information retained for agency use will be sensitive if not classified in the military sense. The field enforcement officer must respect the confidentiality of any information so designated by the refinery management. Any process, control, or cost data that the company feels is proprietarymust be treated as such by the air pollution control agency representative.

B. FORMAT OF RECORDS

Data management and records control procedures may be different at each refinery. It is necessary, therefore, to arrange with

Date ______________

	12-8	8-4	4-12
Time Wind Direction			


N
N St.
Cross Ave.
Frank Ave.
M St.

Remarks

12-8	8-4	4-12

Odor Complaints
From: ______________
Time: ______________
Investigation: ______________________________
____

Figure 78 - Odor survey form

refinery management for the maintenance of data in the format most useful for air pollution control field personnel. In general, written files should contain the following information:

1. Period of Time Covered

Continuous records, such as daily logs, are usually prepared by shift, i.e., 12 to 8, 8 to 4, and 4 to 12 for specified dates. Incident records must accurately pinpoint the time of day, duration of the occurrence, and date. Weekly, monthly, quarterly, and annual records or data summaries must note the time span from start date to end date.

2. Person Responsible for Keeping the Records

Most refineries have designated a member of management to be contacted by the field enforcement officer and to serve as the coordinator for all environmental control functions. Generally, this individual will also be responsible for keeping the records. Since there is the potential for inspections at off-hours and over weekends, supernumeraries who are familiar with the environmental files should be assigned to be contacted during these times.

3. Brief Description of Process or Equipment for Which the Record is Maintained

There are two basic methods for describing the processes or equipment for which data are recorded. The first is to use commonly accepted nomenclature accompanied by a location indicator such as "Fluid Catalytic Cracking Unit No. 1." The second appropriate approach to process identification is a numbering system. Some of the options available include air pollution control agency permit numbers, source registration number or an "Emission Point Number". These designators may be assigned to each point within a refinery capable of emitting air contaminants. A numbering system starting with 001 and continuing until all points are numbered is acceptable.[2] When a numbering system is employed, the descriptive details of the equipment and location must be kept in a master file.

4. Data

Recorded information will generally be presented as a narrative or in tables. Typed data are always preferred but carefully written or printed details are acceptable. Each chart or table should have an appropriate heading to describe the data, i. e., "Hydrocarbon Losses from Tanks", "Semiannual Sulfur Emission Balance", or "SO_2 Losses from Emergency Flaring". Column headings for tabular information should be precise, clearly defined units (such as Bbl/day, Tons/hr, etc.), allow space for remarks and identify totals and subtotals where applicable.

A significant quantity of information is stored in computer data banks. Printouts of these data may use abbreviations to conserve file space. These abbreviations may not be easily understood by the field enforcement officer so it is advisable that descriptions of the abbreviations and symbols be kept with the hard copies.

C. TYPES OF RECORDS

1. Permit or License Files

The field enforcement officer will probably use the permit records more than any other single file. During routine inspections, he observes refinery operations for compliance with permit conditions and looks for equipment or process modifications. Permit certificates may only partially describe a given unit, but additional details are necessary for an efficient inspection. "As built" drawings and flow charts will provide the necessary details to show the field enforcement officer if unregistered modifications have been performed. Each permit unit description should provide operating data[3] which includes throughput, sulfur content of processed crude, fuel usage, or rated capacity.

2. Maintenance Records

Maintenance procedures and schedules including preventive maintenance are essential for a sincere air pollution control effort. Maintenance is not only the repair or replacement of valves, flanges, compressors, etc., after failure; it is a planned, co-ordinated effort to prevent breakdowns which will affect pollutant emission rates. Since maintenance in most refineries is a planning function based upon inputs from the operating departments, replacement, repair and modification schedules will be kept in the planning department files. The field enforcement officer should determine where these records are kept, and who is responsible for the data. Periodically, he should discuss the maintenance and replacement schedules with designated personnel. Often the maintenance plans also include modifications or system alterations for which new permits will be required. A thorough review of all such proposed modifications may preclude legal action at some future date for noncompliance.

Another group of maintenance records which is of concern to field personnel is monitoring instrument repair and replacement. Chapter IV contains a detailed discussion of in-stack and peripheral monitoring systems. Maintenance responsibility for these instruments may reside with the planning department of the refinery, a special instrument repair shop, or the environmental control office. The field enforcement officer must determine where the records are maintained and institute a regular evaluation of the plans for repair, installation, or modification of the instruments.

3. Shutdown and Startup

Reports of equipment malfunctions, upsets, and overload conditions reported by operating personnel should be compiled, recorded and maintained in the environmental control office. As an example, if sulfur recovery facilities are unable to receive the sulfur bearing gases, the gases must be flared causing the release of significant quantities of SO_2. The record of this event will contain the quantity of sulfur burned (usually in tons), the duration of the procedure, time of day and date.

Emergency plans and procedures also come under this category of data. Shutdown procedures for refinery operations call for very stringent safety precautions for both personnel and equipment which are the overriding consideration in the suspension of operations. This coupled with the possibility of secondary effects of greatly increasing emissions demands that curtailment plans be very specific regarding operations and time. The plan is a narrative with accompanying schedules, designated responsible personnel and special safety precautions. The plan must be periodically reviewed by management and agency field officers to assure the workability of the procedure.

4. Ground-Level Perimeter Monitoring and Continuous Source Monitoring Records

The design and placement of ground-level perimeter and continuous monitoring systems are discussed in Chapter IV. Measurements are recorded in analog form on strip or circular charts, in digital form on punched or magnetic tape, or are hand logged from dials and gages. Contaminants monitored are aerosols and gases that are reported in the following manner.

a. Particulates - The ambient measurement reporting units depend upon the sampling or monitoring methods. In the case of a high volume sampler, the units are usually mass concentration units such as mg/m^3. In the case of sequential filter tape samplers, the reporting parameters normally are in reflection or transmittance units such as RUDS (Reflective Units of Dirt Shade) or COH (Coefficient of Haze). These units are arbitrary and cannot be translated directly into mass units unless a consistent conversion factor has been determined. It is not likely that LIDAR or nephelometers will be encountered, but such instruments essentially look at numbers of particles, and reporting units are usually in terms of visibility.

In the case of a source monitoring instrument, the recording is actually a fraction or percentage of the full-scale range of the instrument. Only if the instrument has been calibrated and a scale attached to the instrument can a meaningful reporting parameter be observed. Further, most monitoring devices measure concentration so that stack exhaust flow must be known before mass per unit time such as lbs/hr can be derived. The most common particulate monitoring device that will be encountered will be an opacity meter. These instruments are usually calibrated to give a direct readout in terms of opacity. In some cases, they may be calibrated in terms of mass concentration units such as gr/ft^3, mg/m^3, etc. The new beta gage-filter tape samplers are calibrated to read out directly in mass concentration units.

b. Gases (SO_2, H_2S, NH_3, NO_x, Amines, RSH) - Monitoring for gases almost uniformly results in the reporting units being produced in volumetric concentration units. Depending upon the concentration these units may be percent by volume, parts per million (ppm), or even parts per billion (ppb). Most instruments would be calibrated to permit the use of a direct-reading scale. In some cases where a multirange instrument is used, the scale would be only in percent of full scale.

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VI. ESTIMATING AND ASSESSING EMISSIONS

A. INSPECTION AND SURVEILLANCE PROCEDURES

An air pollution inspection consists of entering a refinery to determine if the equipment or processes meet the standard and comply with the rules and regulations of the air pollution control agency.

Some inspections, especially initial ones, are comprehensive and designed to gather information on all equipment and processes of the refinery. Others are conducted for specific purposes, such as:

- obtaining information for source registration;
- gathering evidence relating to violations;
- checking permit or compliance plan status of equipment;
- investigating complaints;
- following up on a previous inspection;
- obtaining emissions information by source testing.

Field surveillance is a field operations activity that provides for the systematic detection and observation of emission sources. Observations are made of surrounding areas and the exteriors of facilities for visible emissions, odors, contaminant damage, new construction or expansion, and other visual or sensory manifestations of air pollution or changes in emission potentials.

Surveillance is conducted mostly by vehicle patrol. However, aircraft, television, ambient air-sampling devices, and pollutant-detection instruments can be used.

An initial refinery inspection lays the groundwork for evaluating potential emissions of pollutants from a facility and for assessing the relative magnitude of pollution control problems requiring correction, reinspection, or further attention.

The initial inspection has two phases: a refinery survey and a physical inspection of the equipment and processes. After this inspection is complete, routine surveillance continues. Periodic reinspections are scheduled and occasional special-purpose inspections (unscheduled) may be required.

1. Initial Refinery Survey

The elements of a refinery survey include:

- Environmental Observations - the examination of possible effects of emissions on property, persons, and vegetation adjacent to the source; include the collection of samples or specimens that exhibit possible pollution-related damage.
- External Observations of Facility - observation of all possible points of emission, all visible emissions, odors, and pollution-related activities.

- Management Interview - interview with refinery managers and equipment operators establishes corporate identity, ownership of the organization, operations, and air pollution control performance.
- Process and Equipment Inventory - the inventory consists of obtaining complete descriptions and records of all processes equipment capable of emitting air contaminants. The inventory inspection can also serve to initiate a source registration system as a method for rigorously accounting for equipment and processes capable of air pollution or confirm the information provided in permit applications.

a. Environmental Observations - The surroundings of any refinery or petroleum operation should be surveyed for odors and for damage to vegetation and materials. Findings should be confirmed by questioning residents in the neighboring communities. Soiling of surfaces of automobiles, residences, and other structures should be noted and, where found to be severe, should be investigated. Any pattern of increasing intensity of soiling or staining of materials in the immediate vicinity may be a clue to previously unrecognized emissions and should be studied.

Hydrocarbon vapors and gases are likely to be particularly prevalent near petroleum production and refining facilities. When the odors are intense, they indicate the occurrence of high emission levels since odor thresholds for these compounds are relatively high and their quality not especially offensive.

Sulfur compounds associated with crude oil production and with some refinery operations are readily detectable by odor. Sulfur dioxide may be produced by combustion of fuels or waste gases (for example in boilers, catalyst regenerators, incinerators, and flares). This gas has an acrid, suffocating odor with a threshold at one part per million (1 ppm). Reduced sulfur compounds, including hydrogen sulfide, various mercaptans, and other sulfur-bearing organics, have characteristically very offensive odors and very low threshold levels, which have been estimated at less than one part per billion (1 ppb).[2]

In reporting on occurrences of odors allegedly caused by petroleum facilities, the inspector should note wind conditions (speed, as well as direction) at the time of his observations, and he should develop systematic procedures for patrolling and characterizing odors.

Odors may be described on an intensity scale in terms of subjective evaluation, or a procedure using a scentometer or other comparison devices may be adopted. A community odor panel can help to establish the significance of day-to-day variations in odor intensity and quality of the ambient atmosphere, as well as to alert the field enforcement officer to the occurrence of unusual conditions.

Sulfur compounds, particularly hydrogen sulfide, can discolor and damage lead-based paints often used in residential areas. They also accelerate tarnishing of silver and copper surfaces.

Sulfur dioxide and trioxide may be responsible for causing damage to vegetation, such as evidenced by yellow to brown blotchy spots on many varieties; sulfuric acid mist formed from the trioxide occasionally causes a sort of pock-marking injury to plants. Diagnosis of plant damage due to air pollutants is difficult, however, and should be confirmed by consultation with someone experienced in the field.[3]

Data relevant to determining the speed and direction of dispersion of contaminants in the atmosphere include temperature, humidity, wind speed, and wind direction measurements. These data are continuously provided at weather observing stations, but they may be required at other locations during special investigations.

Equipment suitable for such purposes includes thermometers, psychrometers, especially the "sling" variety and anemometers or wind gages. Such equipment is discussed in detail by Hewson.[4] For measuring surface wind speeds, rotation anemometers are most satisfactory; a particularly convenient type is the totalizing cup anemometer, which counts and records each tenth, sixtieth, or whole mile of wind past the instrument.

b. External Observations of Facility - A fundamental inspection technique consists of identifying, describing, and evaluating air pollution emissions and the factors contributing to their formation.

The field enforcement officer must demonstrate that his observations prove the presence of an air contaminant (that is, an effluent that is not water vapor or a natural constituent of the atmosphere) and that the emission violates a standard. He must also determine what factors caused the emission to violate the standard. He should be prepared to describe the events occurring in each stage or element of the air pollution problem.

(1) Visible emissions (plumes) - The air contaminant of primary interest is the plume. It is the "discharge" or "emission" regulated or prohibited in most statutes or rules.

Since all substances become liquid, solids, and gases at certain temperatures, the plume may consist of a variety of contaminants in various states of matter. Smoke, for instance, contains visible aerosols - carbon particles and solid or liquid particles of partially burned fuels - gases such as sulfur dioxide, oxides of nitrogen, and unburned vapors.

The identity ascribed to the plume is usually made in terms of its outstanding visible characteristic. For example, even though sulfur dioxide may be the most significant of the pollutants emitted from a given stack, the effluent in which it is contained is frequently described as smoke due to the visible soot, carbon particles, and fly ash contained in the plume.

The mere observation of a plume, however, does not result in its conclusive identification. Knowledge of the specific conditions which caused the contaminants is required. The distinction between smoke and fumes cannot be made unless the processes by which they are generated are known. Effluent plumes may be smoke, dusts, mists, gases or vapors.

- Smoke is the visible effluent resulting from incomplete combustion. It consists mostly of soot, fly ash, and other particles less than one micrometer in diameter. Depending upon the composition of the fuel or materials being burned and the efficiency of combustion, various volatilized gases and organics such as aldehydes, various acids, sulfur oxides, nitrogen oxides and ammonia may also be emitted. Because of the low vapor pressures and slow settling properties of the particles, the smoke may be carried considerable distances from the source and many submicron particles will be permanently dispersed in the atmosphere.

Smoke will vary in color but will be generally observed as grey, blue, black, brown, white, or yellow, depending upon types of fuel or material and the conditions under which they are burned. The color of smoke is generally a good indication of the type of combustion problem encountered.

Grey or black smoke may indicate that material is being burned with insufficient air or inadequate mixing of fuel and air. This, for example, will occur during the flaring of waste gases when steam injection is not functioning properly.

- Dusts are minute solid particles released in the air by natural forces or by mechanical processes such as crushing, grinding, melting, drilling, demolishing, shoveling, sweeping, and sanding. Dust particles are larger and less concentrated than those in colloidal systems, such as smoke and fumes, and will settle fairly quickly on surfaces. A dust effluent may also contain many submicroscopic particles.

Catalyst regenerators are a major source of dust emissions in refineries. High efficiency collection systems such as electrostatic precipitators in series with cyclones or multiple cyclones in series are generally used to control this pollutant. Bag filters are not generally used in petroleum refineries though baghouses may be required to meet stringent air pollution control regulations.

- Mists consist of liquid particulates or droplets smaller than raindrops, such as fog, and are formed by condensation of a vapor or atomization of a liquid by mechanical spraying. Mist droplets may contain contaminant material in solution or suspension.

In large oil-burning installations, sulfur trioxide is formed as a gas and, after contact with sufficient moisture in the air, forms as a white-to-blue plume several feet above the stack (detached plume). After further contact with moisture in the air, the sulfur trioxide is transformed to a sulfuric acid mist.

- Gases - A gas is a fluid of freely moving molecules tending to expand infinitely and to diffuse and mix readily with other gases. Gas pollutants include a large variety of inorganic and organic compounds which may have noxious, malodorous, toxic or corrosive effects or may have an effective smog-producing potential. These include carbon monoxide (CO), ozone (O_3), oxides of nitrogen (NO, NO_2), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), hydrocarbons and their oxidation products, halogens (chlorine, bromine, fluorine, iodine) and their derivatives such as hydrogen fluoride (HF), and various chlorinated solvents such as those used in industrial degreasing and dry cleaning. Other important toxicants include ammonia (NH_3), arsine (AsH_3), fluorine (F_2), hydrogen chloride (HCl), phosgene $COCl_2$) and hydrogen cyanide (HCN).

Gases that commonly occur in refinery air pollution problems as a result of direct emission are sulfur dioxide, hydrogen sulfide, and mercaptans.

- Sulfur dioxide is a common stack gas produced from the combustion of sulfur-containing fuels such as coal and fuel oil, the burning off of residue on catalyst in oil refining operations, the burning of tail gases from the recovery of sulfur from refinery waste gases, and various other chemical and metallurgical processes. A major source of sulfur dioxide is the burning of fuel oil by refineries. Fuel oil may have a sulfur content from less than 1 percent sulfur to 5 percent in some of the heavier fuels. SO_2 has a noticeable odor at comparatively low concentration and will damage certain species of vegetation at 0.25 ppm. Sulfur dioxide gases and sulfuric acid mists can hasten the corrosion of wires, metals, and other materials.

Cracking processes in oil refining operations convert the sulfur contained in the crude oil into hydrogen sulfide and mercaptans. When hydrogen sulfide is released to the atmosphere as a gas, it manifests a characteristic rotten egg odor. From relatively small gas concentrations, mercaptans also exhibit strong unpleasant odors such as garlic, decayed garbage, skunk, or onions. Hydrogen sulfide is detectable at 0.12 ppm and mercaptans at 0.001 to 0.041 ppm. Under humid conditions, H_2S will also discolor some surfaces painted with lead pigments.

- Vapors - A vapor is the gaseous phase of a substance which at normal temperature and pressure is a liquid or solid.

The most important vapor problem results from the evaporation of petroleum products, such as the unburned gasoline vapors in automobile exhaust. Gasoline vapors also originate from processes in which volatile products are maintained in storage tanks and from the operation of pumps, compressors, and blowers required for moving liquid and gas streams.

(2) Evaluation of visible emissions - Once a plume is identified as an air contaminant, it must be measured against some standard to determine whether a violation of the law has occurred or it must be evaluated to determine the size or severity of the pollution.

Compliance with applicable emission standards is determined by visual evaluation of visible emissions and by source testing of emissions which are invisible or near the threshold of vision.

Visual observation of plumes by field personnel can be an effective and economical method of determining compliance with air pollution regulations, provided the regulations are based on the visible aspect of plumes or on other properties that can be shown to be directly related to the visible aspect.

The benefits of basing smoke statutes on opacity or density are quite evident, even though equipment and fuel regulations have increasingly assumed precedence in control legislation. When the visual standard is specific with reference to a cut-off point and time interval, it is simply and directly enforced. To cite a violator for excessive smoke, enforcement officers need only observe an emission of an opacity or density beyond that allowed for a specific period of time. Although the visual standard is limited to estimations of particulate pollution which obscures vision, its application simultaneously tends to reduce grain loading and gaseous contaminants. (As the grain loading in the plume increases, the light transmission decreases exponentially.) To comply with the opacity standard, more efficient combustion or equipment operation is necessary. The Ringelmann standard can be applied not only to smoke, but to fumes, dusts, and mists arising from a variety of problems and, therefore, is most versatile in identifying and controlling atmospheric pollutant emissions in a community.

However, while large reductions can be anticipated, they cannot always be precisely predicted or evaluated. Determination of opacity and shade of any emission alone gives no specific measurement of the quantities of contaminants being emitted.

A complete description of the theory and use of the Ringelmann chart is discussed in a Bureau of Mines Information Circular[5] and in EPA Field Operations Manual[6].

(3) Investigation of odor potentials of emission sources

- Plant Inspection[7] - On suspicion of odor nuisance emissions, an inspection may be undertaken supplemented by source testing for evaluation of the odor potential. As soon as practical after identifying the suspected source of odor emissions, the field officer should enter the refinery: (1) to gather the evidence needed to prove that the violation has occurred, for example, that someone discharged into the atmosphere, a contaminant in greater amount or density than allowed and for more than the specified time; (2) to determine the cause; and (3) to ascertain the necessary corrective measures.

By proper interrogation, the field officer should establish the circumstances leading to the emission violation. He should be alert for observations he can make to verify the accuracy of the statements made to him.

Next, if not already a part of the plant record, the equipment data are obtained. These should include the make, type, size, and capacity of all equipment or processes involved. General conditions bearing on the air pollution potential of the equipment should be noted. Observations should be made of gages and monitoring instruments, particularly temperature charts on incinerators, and load charts on boiler instrument panels. Information on operating failures which lead to excessive emissions is being published in the technical literature. Much can be learned from process studies which identify operating conditions that cause high pollution discharge.

- Evaluating Odor Concentrations - If the odor being investigated has been identified as caused by a known odorant, its concentration should be measured by chemical or physical means in the laboratory. This is especially true when the known odorant also has toxic or irritant potential, as in the case of hydrogen sulfide, sulfur dioxide, ammonia, chlorine, and various aldehydes. In many such cases, the criteria for acceptable concentrations in ambient air are already established in terms of mass concentrations which are lower than odor thresholds, so that evaluation in terms of odor units is superfluous.

However, when the odor nuisance is the only suspected effect, or the identity of the odorant is in doubt, or more specific methods of measurement are unavailable, the samples collected at the source should be evaluated by an odor panel using dilution techniques.[8]

(4) Relating source strength to control requirements - The contaminants responsible for an odor should be controlled so that threshold levels are never reached in the outdoors. Some industries assume that they have no odor problems, because they consider discharges from their processes to be unobjectionable or even pleasant. However, the presence of any odor which persists and is not normally associated with the daily routine of living will be a source of annoyance to the neighborhood.

The odor evaluations of source samples provide estimates of odor concentrations in terms of odor units per unit volume. These estimates can serve as guidelines in the develment of control methods. Thus, if a stack effluent is normally diluted by a factor of 1,000 before it arrives at a breathing level in the surrounding neighborhood, an odor concentration of 1,000 odor units per standard cubic foot could be considered to be on the verge of acceptability, while an odor concentration of 10,000 would require at least 90% control.

This sort of guideline can be refined by calculating an odor emission rate in odor units per minute. This is equal to the product of the odor concentration and the volume rate of the stack exhaust, in standard cubic feet per minute.

Dilution factors required for positive control can be estimated either by surveying ambient air in the vicinity to determine the maximum odor concentrations observable or by standard engineering design procedures based on plume dilution equations or community experience. It should be remembered that dilution of odorous gas to the median odor threshold level can be expected to render it undetectable by only about half of the people in the community: therefore the use of an additional safety factor in design for positive control is advisable. Also, dilution factors work better near the source and tend to break down with distance.

An application of odor measurement in improving neighborhood odors would be to survey all the operations in a plant and determine the odor emission rate from each. Listing such emissions together with estimates of costs for control can help management pick out the largest odor sources (rather than the largest stacks or largest volume discharges) and concentrate effort initially on those which are likely to provide the greatest improvement per dollar of expenditure.[9]

c. Management Interview - The purpose of the management interview is to obtain from management and supervisory personnel the identification of processes and equipment as possible sources of pollutant emissions, preparatory to making the detailed equipment inventory.

In particular, the field enforcement officer should obtain:

- business and ownership data, including former owners, and responsible management personnel
- plot plans showing disposition of all major units of the facility
- flow charts for each major processing unit, indicating purpose, operating conditions, and normal processing capacity.

The FEO should determine what procedures are employed to control or eliminate the discharge to atmosphere of noxious or malodorous emissions through the purging or depressurizing of tanks or vessels. These procedures may include the installation of special instrumentation, high-level or high-pressure alarms, liquid knock-out drums on fuel gas systems, pressure relief or manually controlled discharge from process equipment to blowdown vessels of either variable or fixed capacity which are served by vapor recovery compressors, flare systems, or both, and fixed roof tankage tie-in to properly sized vapor recovery or fume disposal systems.

d. Process and Equipment Inventory - The initial process and equipment inventory may be developed from information acquired through administration of a permit system or a source registration system or from direct interviews and conferences with management personnel. It consists of complete records of all equipment and processes capable of emitting air contaminants that are located at all facilities within the jurisdictional area.

Inventory of equipment is called an equipment list. This list enumerates all items capable of emitting air contaminants that are located at a given refinery and the status of that equipment with respect to compliance with the permit system and the rules and regulations.

In preparing equipment lists, the agency should consider using the format of procedures devised by the

Environmental Protection Agency for the National Emissions Data System (NEDS). Equipment and process classifications readily usable for an automated data processing system have been enumerated which may also serve as an aid in preparing equipment lists. Complete details of this system are contained in the EPA Guide for Compiling a Comprehensive Emission Inventory.[10]

2. Physical Inspection and On-Site Testing

a. Preparing for the Plant Visit - The objectives of the field enforcement officer are not only to determine which elements of the operation are governed by rules and regulations, but to determine as well the degree of compliance to them. His inspection procedures are adapted to the specific air pollution regulations that apply to the type of unit being inspected. All refineries have standard safety procedures for employees and visitors. These procedures also concern the field enforcement officers.

(1) Review of records and regulations - Prior to the physical inspection, the field enforcement officer should review and organize the records contained in the field file. He should determine what specific rules and regulations apply to the operations of the facility to be inspected and he should be

prepared to furnish appropriate copies or extracts of these regulations to the management of the facility.

On the occasion of the initial physical inspection, the field file for the facility should contain the equipment list, plot plans, flow charts and auxiliary information furnished by management in the interview phase of the inspection. At this stage, the file will probably be incomplete, and a major objective of the physical inspection is to fill in the gaps and pin-point problem areas. The visit will also be the subject of an Activity Status Report on findings and recommendations.

Because of the operational complexity of petroleum refineries, and allied activities, a degree of specialization, and training and experience is required to make an effective FEO. It is necessary to write technical reports of processes and to prepare graphic presentations to describe the air pollution potentials of the process units being inspected.

Separate inventory forms for each type of equipment, operation, process, and plant are helpful at inspections to ensure coverage of specific points. Coverage is complicated because:

- Similar process vessels are used in various source activities and are grouped interdependently. Attempts to itemize individual pieces of equipment often lead to confusion and disorientation.

- Air pollution potential can be better determined from an inventory of functions of process vessels than from itemization of equipment units. Process inventories may also require field surveys of product flows, throughput capacities, and emission factors.
- Refinery and chemical plant inventories thus categorize, itemize, and present such data as will directly determine compliance not only with permit regulations but also with equipment regulations.

To make these data readily available, a special inventory system should be adapted for each refinery. To cover each of the multiple operations of a refinery adequately, the plant area is subdivided into process units. (Units with the greatest air pollution potential are subsequently assigned more frequent inspections.)

Plant ownership data is recorded separately on a Plant Card. It is most important to know who the responsible officials are and how they can be quickly contacted. Where accurate field data exist in the inventory files, it is possible to make a preliminary investigation of refinery problems by telephone.

The inventory records for each refinery consist of a group of file folders, each folder dealing with a single process unit. The folders are numbered and filed sequentially. As one or more process units may constitute a source activity, an index of source activities cross referenced by folder number is maintained at the head of the file.

A source activity folder contains:

- A general description of the process and an analysis of its purpose and function in the processing sequence. Generally, the analysis traces the flow of materials from introduction through various sidestreams to final effluents.
- A list of pieces of equipment contained in the process unit and their function.
- A discussion of the air pollution potential of the process or equipment including an analysis of any important problems and, if possible, estimates of the contaminants emitted and their chemical designations, odor quality and intensity, opacities, or physiological effects, as well as the potential hazards of the stocks or products released should equipment failure occur.
- Estimates of throughput of volatile materials and of emissions from known sources. This may be determined from results of "material balances", e.g., estimates of sulfur derivatives lost as calculated from the differences between input and final output.
- Results of any tests or analyses of effluents, fuels or other materials.

- A process flow chart and plot plan, which can be used for reference and verification on follow-up inspections. These give the flow rates, pressures, temperatures, etc., in process vessels and lines, where necessary to estimate air pollution potential and to locate points of emission.

Flow diagrams and plot plans are of particular importance in accounting for all equipment in a production sequence which otherwise might be overlooked. They are of value in showing the potential of an existing production system for growth or change. They also show the capacity for such systems to accomodate increased production. Comparison of the flow chart and plot plans with conditions existing at a later inventory reinspection will show exactly how the process may have changed.

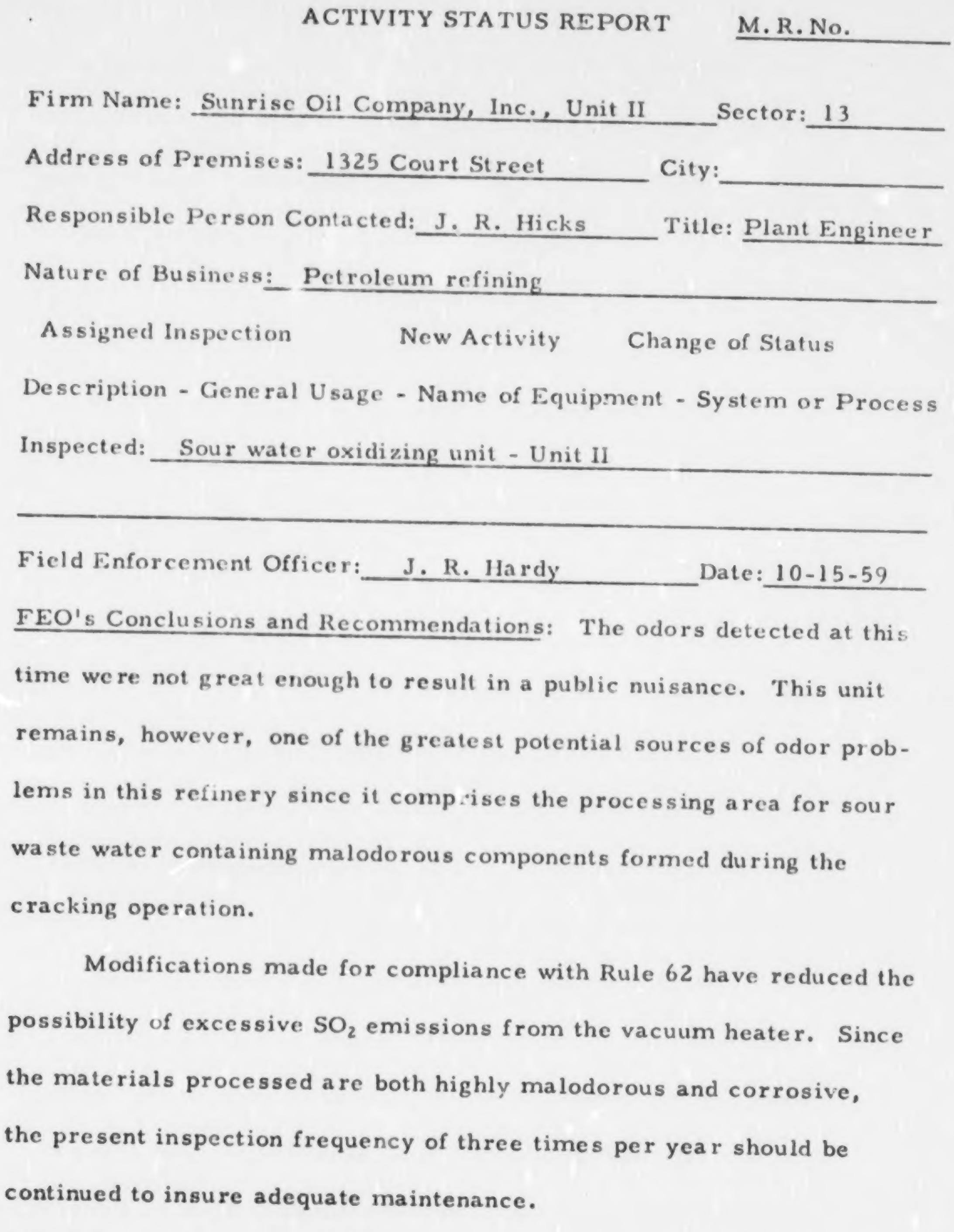
Flow charts and plot plans are drawn according to conventional engineering rules. Pertinent liquid or gas feed lines are shown and gas or liquid effluents indicated. Overhead discharge and drainage from columns or vessels are generally shown by vectors indicating method of disposal. Features not essential to the understanding of the air pollution problem are omitted.

The flow lines are clearly labeled and vectored as to direction and content, for example: "Refinery Gas In", "To

Fuel Gas System", and "To Oil-Water Separator". The process lines indicate whether the flow originated in, or entered at the top, side, or bottom of columns or equipment. Functions of equipment and columns should be clearly labeled, unless they can be depicted by symbols (such as heat exchangers, and condensers, and by plant number). It is of utmost importance in a flow diagram to illustrate clearly all sources of air pollution, including stacks, flares, and pressure relief valves, and to identify the problem areas and the contaminants which may be emitted. Process vessel and line operating conditions recorded on pressure and temperature gages, manometers, continuous recorders, and relief valve pressure settings should be indicated wherever pertinent.

A sample of an Activity Status Report covering a sour water treatment and disposal plant and accompanying flow charts are shown in Figures 79 and 80. The symbols used in chart preparation are shown in Figure 81.

Some sources are so routine that standard inventory forms are used to report them. These include bulk plants, truck loading facilities, oil-effluent water separators, tanks, and natural gasoline plants. Examples of these forms and the Activity Status Report are those used by the Los Angeles County Air Pollution Control District.



ACTIVITY STATUS REPORT M. R. No. ____

Firm Name: Sunrise Oil Company, Inc., Unit II Sector: 13

Address of Premises: 1325 Court Street City: ____

Responsible Person Contacted: J. R. Hicks Title: Plant Engineer

Nature of Business: Petroleum refining

Assigned Inspection New Activity Change of Status

Description - General Usage - Name of Equipment - System or Process

Inspected: Sour water oxidizing unit - Unit II

Field Enforcement Officer: J. R. Hardy Date: 10-15-59

FEO's Conclusions and Recommendations: The odors detected at this time were not great enough to result in a public nuisance. This unit remains, however, one of the greatest potential sources of odor problems in this refinery since it comprises the processing area for sour waste water containing malodorous components formed during the cracking operation.

Modifications made for compliance with Rule 62 have reduced the possibility of excessive SO_2 emissions from the vacuum heater. Since the materials processed are both highly malodorous and corrosive, the present inspection frequency of three times per year should be continued to insure adequate maintenance.

Figure 79. Activity Status Report from an Inspection Made of a Sour Water Oxidizing Unit at an Oil Refinery (from Los Angeles County Air Pollution Control District).

FEO's Findings: The purpose of this unit is to deodorize the sour water pumped from the accumulators at the crude, thermal, and catalytic cracking units. This consists of the following equipment:

(1) a 10,000 barrel cone-roof tank, (2) a neutralizing column tower, (3) a waste-water stripper, (4) an aeration column, (5) a waste-water cooler, (6) a sour water degasifier drum, and (7) necessary pumps, piping, and instrumentation. These are shown in the attached flow diagram.

The sour water is pumped from the accumulators to the degasifier drum. The gas removed from this drum flows through a back pressure regulator valve to a low pressure H_2S removal plant.

The sour water and waste caustic are collected in the 10,000 bbl. capacity tank venting to the vapor recovery system.

The sour water is pumped from the tank to the neutralizing column where it contacts 98% sulfuric acid. The mercaptans released from the water by the sulfuric acid, along with other waste gases in the overhead line from the caustic regeneration unit, are condensed and fed into the cracking unit for conversion to H_2S and recovery. This accounts for the disposal of most of the mercaptans in the system.

The neutralized water is then pumped to the waste-water stripper, and live steam is introduced in the column to strip out H_2S and mercaptans. Sweet gas with 7 or less grains of H_2S per 100 CF

Figure 79 (continued) Page 2 of 4.

from the secondary scrubber at the H_2S removal plant is introduced into the bottom of the stripper at the rate of 350,000 to 500,000 CF/D to sweep the released gases from the water. This sour gas from the stripper goes to the H_2S absorption plant. A pressure relief valve on the stripper vents to the flare.

The stripped water then flows to an aeration column where it is contacted counter-currently with an air stream and caustic and is oxidized to non-odorous thiosulfate. The resulting foul air from this vessel is sent to the firebox of the vacuum unit heater for deodorizing. The water flows from the bottom of the serator through a cooler to the covered waste-water separator.

Prior to the introduction of the air pollution control program, the principle sources of air pollution at this unit resulted from the introduction of (1) mercaptans from the neutralizing tank to the burners of the vacuum unit heater, and (2) the H_2S from the waste-water stripper column to the refinery fuel gas system. The APCD test team determined that previously 0.5 ton/day of H_2S was contributed by this unit to the refinery fuel gas system. This is equivalent to a loss of 2,000 lbs/day of SO_2 to the atmosphere. After studying data disclosed by extensive physical inspection, testing, and industrial cooperation on waste gas streams throughout the refinery, Rule 62 was introduced to control those waste gas streams to be incinerated and

Figure 79 (continued) Page 3 of 4.

containing significant quantities of sulfur derivatives. To comply with this rule, this refinery adopted the following solutions to meet the problems resulting from its particular operating methods:

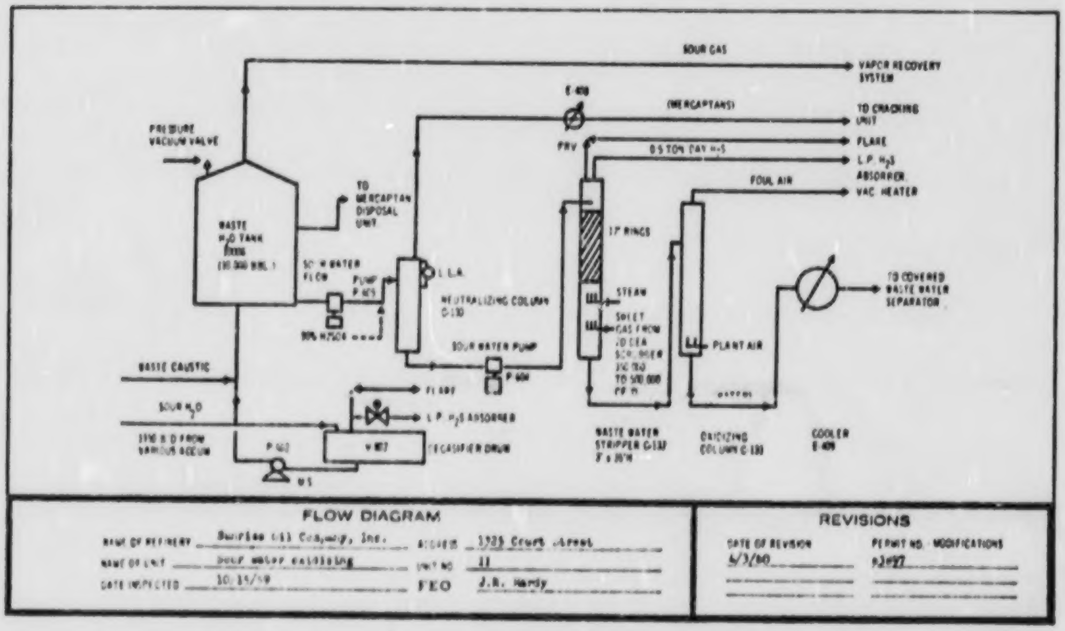
a. Enlarged its H_2S absorption facility.

b. Made provision for introduction of condensable mercaptans into the cracking plant for conversion of H_2S and its eventual recovery.

The waste gas stream now burned in the vacuum unit heater was found to comply with Rule 62 during a test conducted by the APCD test team on 10-13-59.

Negligible mercaptan odors were noted in the vicinity of equipment at this time. Equipment was in good condition and operating under permit conditions and requirements. No visible emissions were observed at this time from the vacuum heater. A sample of treated water taken from the cooler (after oxidation) was free of noxious odors.

Figure 79 (continued) Page 4 of 4.


SOUR GAS
VAPOR RECOVERY SYSTEM
E 410
(MERCAPTANS)
TO CRACKING UNIT
PRV
FLARE
0.5 TON DAY H_2S
L.P. H_2S ABSORBER
FOUL AIR
VAC HEATER
PRESSURE VACUUM VALVE
WASTE H_2O TANK
(10,000 BBL.)
TO MERCAPTAN DISPOSAL UNIT
SOUR WATER FLOW
PUMP P 415
98% H2SO4
L.L.A.
NEUTRALIZING COLUMN C-130
SOUR WATER PUMP
P 404
17' RINGS
STEAM
SWEET GAS FROM 20 DEA SCRUBBER
TO 500,000 CFM
PLANT AIR
TO COVERED WASTE WATER SEPARATOR
WASTE CAUSTIC
SOUR H_2O
FROM VARIOUS ACCUM
FLARE
L.P. H_2S ABSORBER
P 412
V 107
DEGASIFIER DRUM
WASTE WATER STRIPPER C-132
OXIDIZING COLUMN C-133
COOLER E 409

FLOW DIAGRAM

NAME OF REFINERY Sunrise Oil Company, Inc. ADDRESS 3725 Court Street
NAME OF UNIT Sour water oxidizing UNIT NO 11
DATE INSPECTED 10/15/79 FEO J.R. Hardy

REVISIONS

DATE OF REVISION	PERMIT NO. MODIFICATIONS
6/3/80	a2#97

Figure 80. Process flow diagram of a sour water oxidizing unit (page 4 of the Activity Status Report).

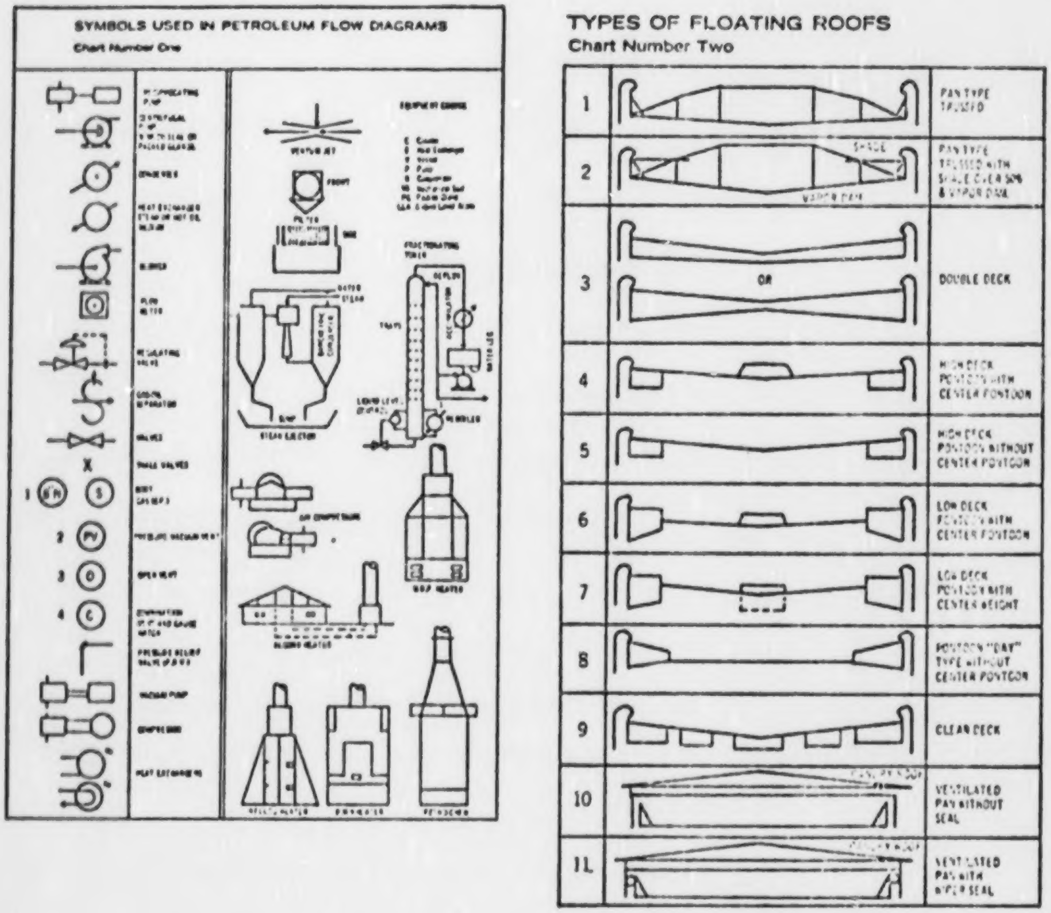

SYMBOLS USED IN PETROLEUM FLOW DIAGRAMS
Chart Number One
FLOW METER
REGULATING VALVE
VALVES
FRONT
FRACTIONATING TOWER
STEAM EJECTOR
X
1
2
PV
3
4
TYPES OF FLOATING ROOFS
Chart Number Two
1
PAN TYPE TRUSSED
2
PAN TYPE TRUSSED WITH SHADE OVER 50% & VAPOR DAM
SHADE
VAPOR DAM
3
OR
DOUBLE DECK
4
HIGH DECK PONTOON WITH CENTER PONTOON
5
HIGH DECK PONTOON WITHOUT CENTER PONTOON
6
LOW DECK PONTOON WITH CENTER PONTOON
7
LOW DECK PONTOON WITH CENTER WEIGHT
8
PONTOON "DAY" TYPE WITHOUT CENTER PONTOON
9
CLEAR DECK
10
VENTILATED PAN WITHOUT SEAL
11
VENTILATED PAN WITH WIPER SEAL

Figure 81. Symbols used in petroleum flow diagrams.

Reproduced from best available copy.

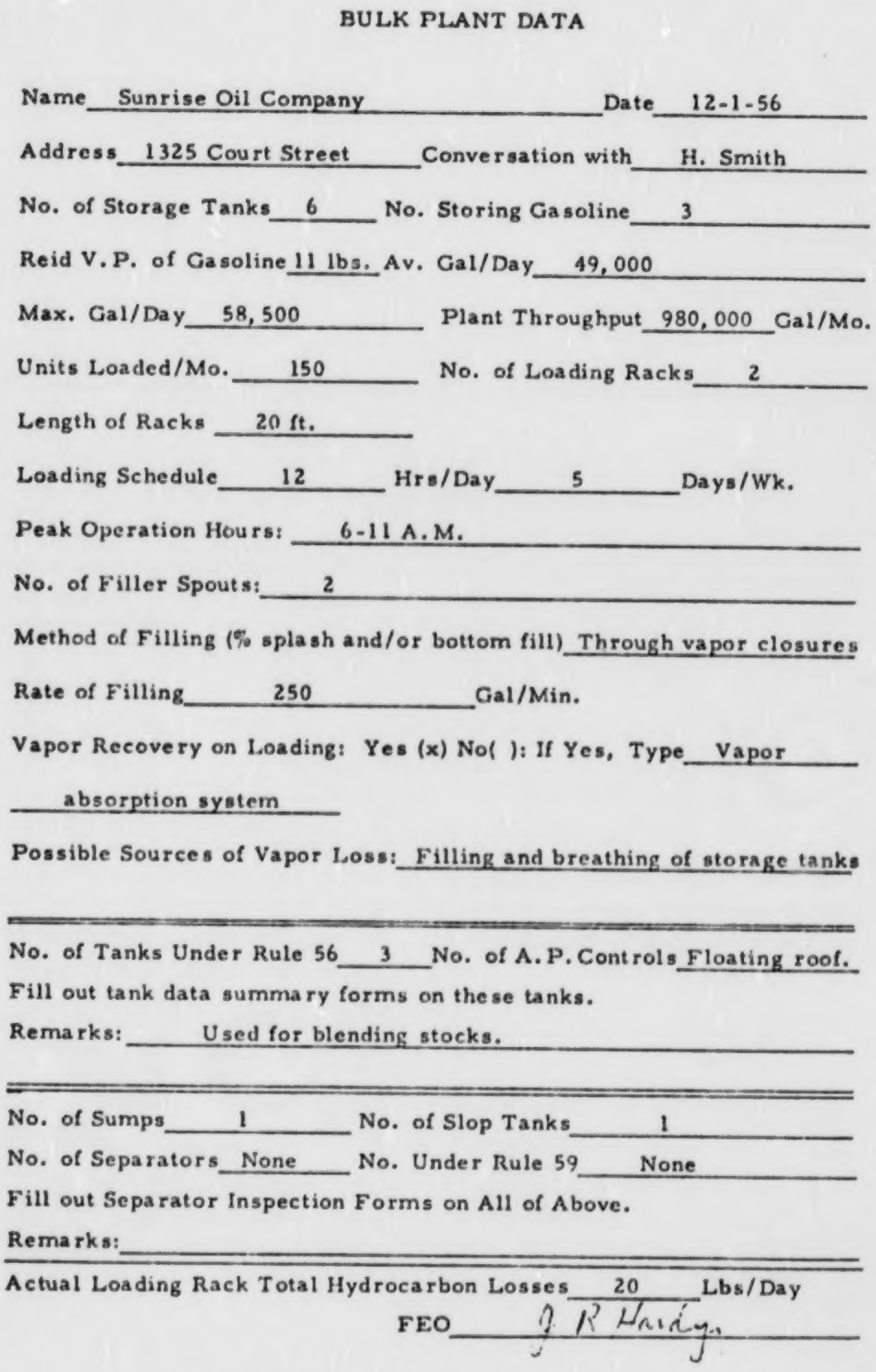
- Bulk Plant Data - This inventory form (Figure 82) is used to record data obtained from inspection of loading racks, storage tanks, pumps, vapor controls, and associated equipment located at bulk plants. Bulk plants are used to store and distribute various petroleum products and may be found at airport facilities, distributing centers, marine terminals, etc. The form is used to emphasize degree of compliance in equipment and operation with the applicable rules. This Bulk Plant Data Sheet presents a master inventory for each bulk plant.

- Truck Loading Inspection Data Sheet - An inspection sheet (Figure 83) is made for each truck loading facility. It lists the number of racks and spouts, the permit status of each rack, and throughputs of tank truck loading racks.

From this form, the total losses of hydrocarbons are determined using the following emission factors:

  - Emission of hydrocarbons in gallons from uncontrolled equipment - Approximately 1/10 of 1 percent of the average gallon throughput per day.
  - Emission of hydrocarbons in gallons from controlled equipment - 8 percent of the above.

- Oil-Effluent Water Separator Inspection - The example shown in Figure 84 is of a single refinery oil-effluent water separator which derives its influent from treating vessels,



BULK PLANT DATA

Name Sunrise Oil Company Date 12-1-56

Address 1325 Court Street Conversation with H. Smith

No. of Storage Tanks 6 No. Storing Gasoline 3

Reid V.P. of Gasoline 11 lbs. Av. Gal/Day 49,000

Max. Gal/Day 58,500 Plant Throughput 980,000 Gal/Mo.

Units Loaded/Mo. 150 No. of Loading Racks 2

Length of Racks 20 ft.

Loading Schedule 12 Hrs/Day 5 Days/Wk.

Peak Operation Hours: 6-11 A.M.

No. of Filler Spouts: 2

Method of Filling (% splash and/or bottom fill) Through vapor closures

Rate of Filling 250 Gal/Min.

Vapor Recovery on Loading: Yes (x) No( ): If Yes, Type Vapor absorption system

Possible Sources of Vapor Loss: Filling and breathing of storage tanks

No. of Tanks Under Rule 56 3 No. of A.P. Controls Floating roof.

Fill out tank data summary forms on these tanks.

Remarks: Used for blending stocks.

No. of Sumps 1 No. of Slop Tanks 1

No. of Separators None No. Under Rule 59 None

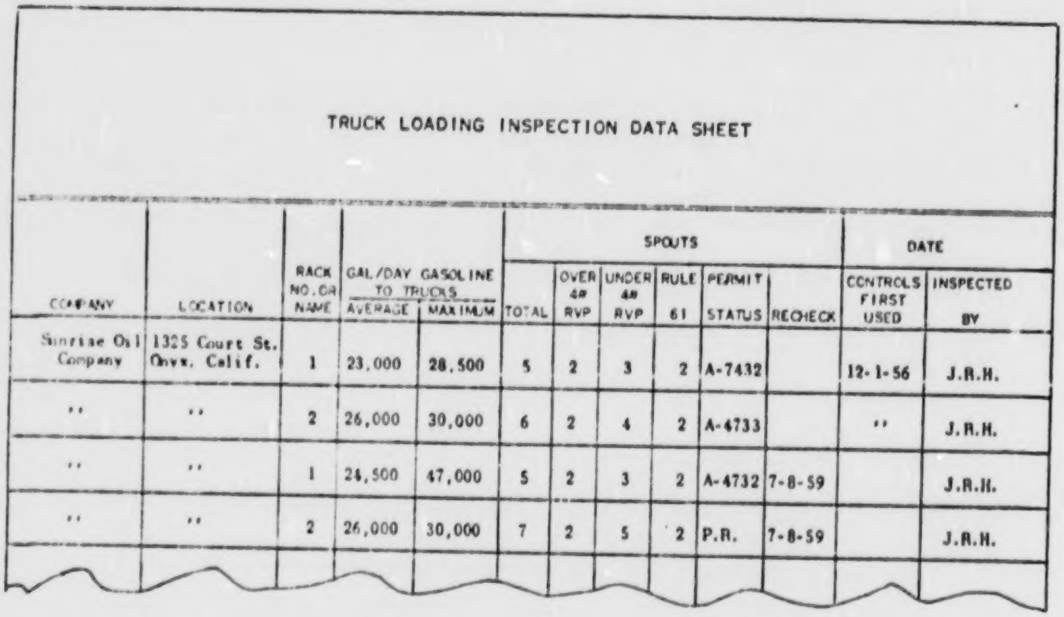
Fill out Separator Inspection Forms on All of Above.

Remarks:

Actual Loading Rack Total Hydrocarbon Losses 20 Lbs/Day

FEO J. R. Hardy

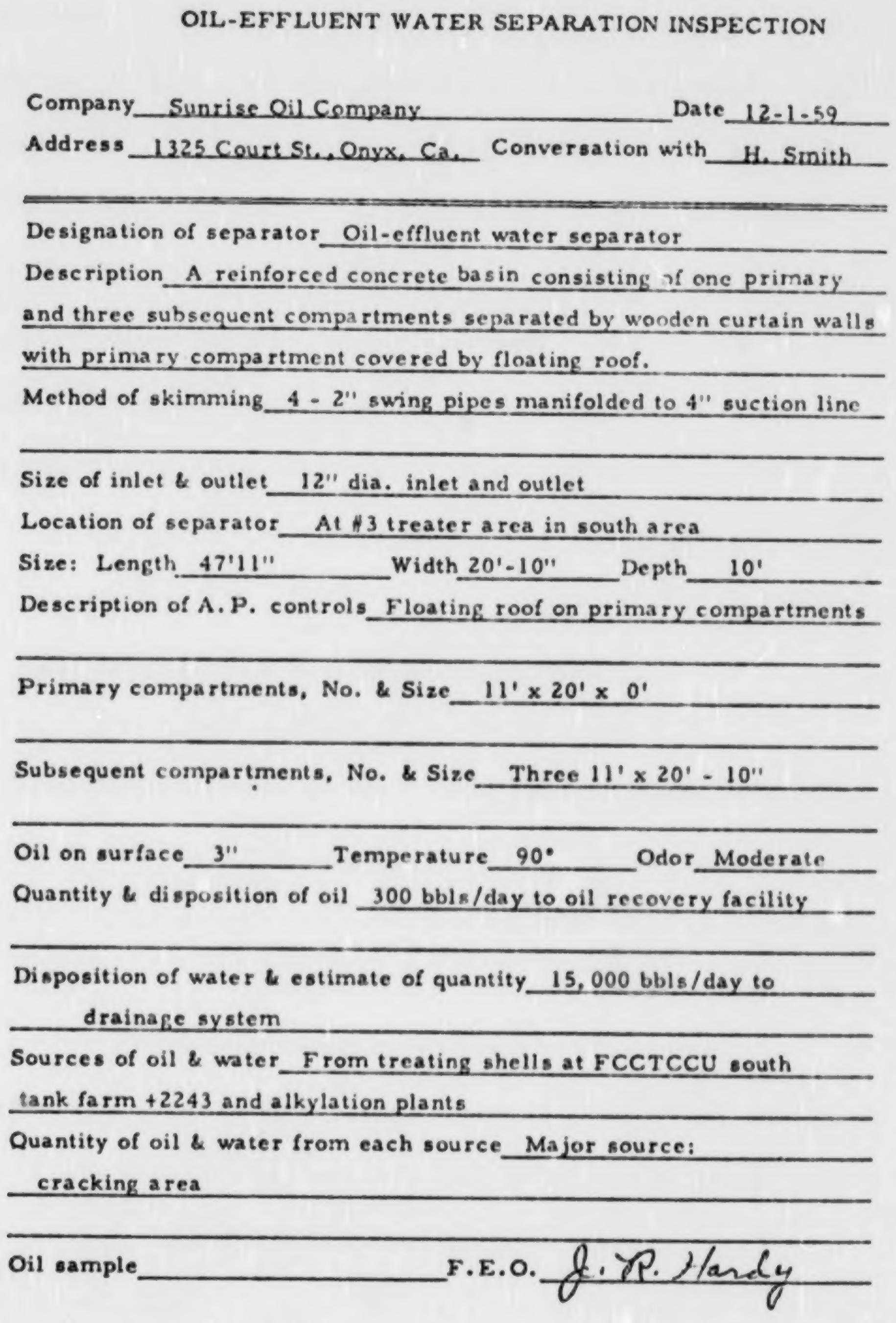
Figure 82. Bulk plant data sheet.



TRUCK LOADING INSPECTION DATA SHEET

COMPANY	LOCATION	RACK NO. OR NAME	GAL/DAY GASOLINE TO TRUCKS		SPOUTS						DATE	
			AVERAGE	MAXIMUM	TOTAL	OVER 4# RVP	UNDER 4# RVP	RULE 61	PERMIT STATUS	RECHECK	CONTROLS FIRST USED	INSPECTED BY
Sunrise Oil Company	1325 Court St. Onyx. Calif.	1	23,000	28,500	5	2	3	2	A-7432		12-1-56	J.R.H.
"	"	2	26,000	30,000	6	2	4	2	A-4733		"	J.R.H.
"	"	1	24,500	47,000	5	2	3	2	A-4732	7-8-59		J.R.H.
"	"	2	26,000	30,000	7	2	5	2	P.R.	7-8-59		J.R.H.

Figure 83. Truck loading inspection data sheet.



OIL-EFFLUENT WATER SEPARATION INSPECTION

Company Sunrise Oil Company Date 12-1-59
Address 1325 Court St., Onyx, Ca. Conversation with H. Smith

Designation of separator Oil-effluent water separator
Description A reinforced concrete basin consisting of one primary and three subsequent compartments separated by wooden curtain walls with primary compartment covered by floating roof.
Method of skimming 4 - 2" swing pipes manifolded to 4" suction line
Size of inlet & outlet 12" dia. inlet and outlet
Location of separator At #3 treater area in south area
Size: Length 47'11" Width 20'-10" Depth 10'
Description of A.P. controls Floating roof on primary compartments
Primary compartments, No. & Size 11' x 20' x 0'
Subsequent compartments, No. & Size Three 11' x 20' - 10"
Oil on surface 3" Temperature 90° Odor Moderate
Quantity & disposition of oil 300 bbls/day to oil recovery facility
Disposition of water & estimate of quantity 15,000 bbls/day to drainage system
Sources of oil & water From treating shells at FCCTCCU south tank farm +2243 and alkylation plants
Quantity of oil & water from each source Major source: cracking area
Oil sample F.E.O. J. R. Hardy

Figure 84. Oil-water separator inspection sheet.

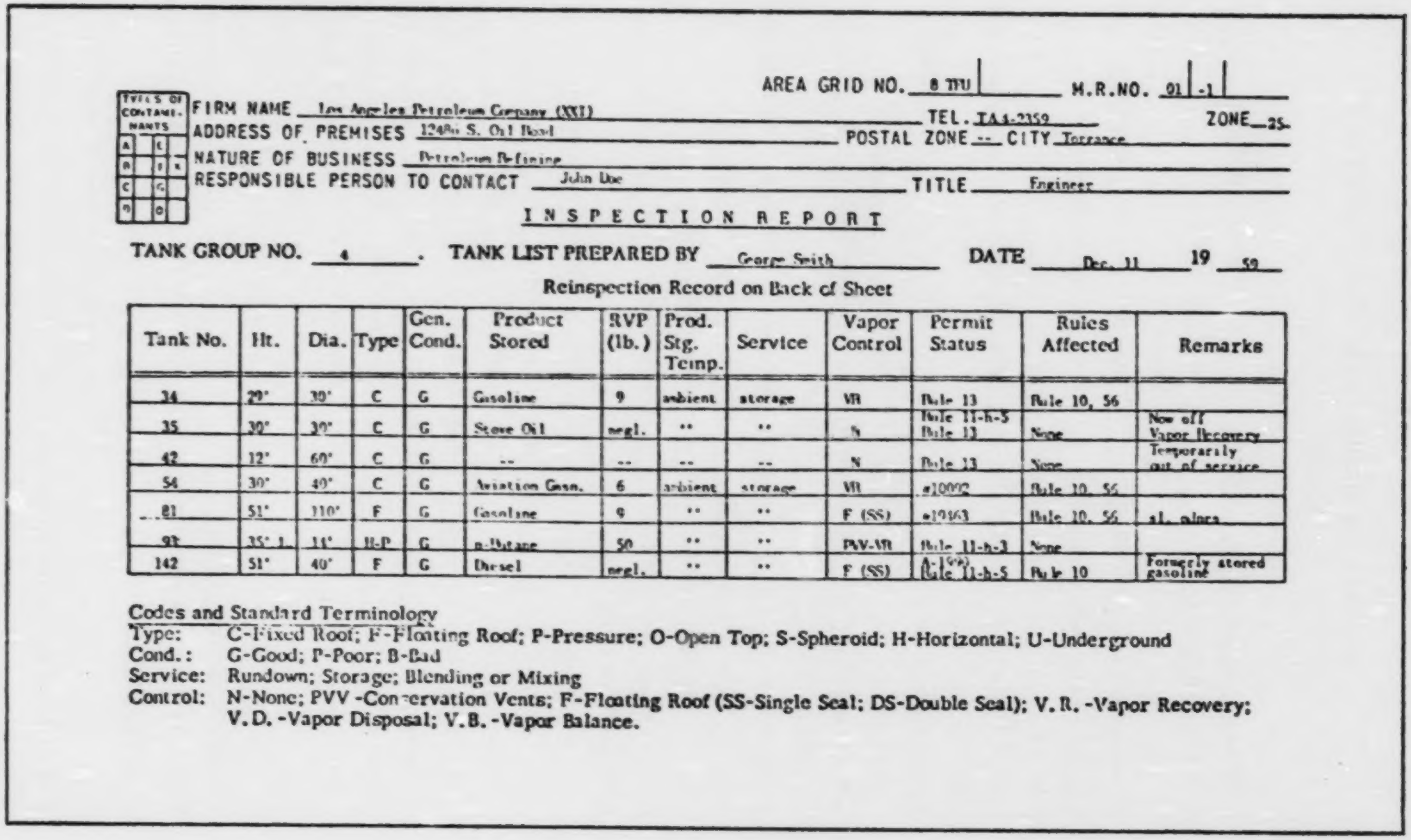
south tank farm, thermal and catalytic cracking units, and alkylation plants in the general cracking area of the refinery. The influent wastewater is traced on the flow diagram by the inspector. The description of the controls, (i. e., "floating roof on primary compartments") and other information indicates whether the equipment is in compliance with pertinent rules.

- Tank Inspection Report - This inventory form (Figure 85) records the type of tank, vapor control, function, dimensions, products stores, Reid vapor pressure, storage temperature, etc., of each tank to determine compliance with rules.

- Data Sheet for Natural Gasoline, Gas, and Cycle Plants - This form (Figure 86) is used to inventory plants located away from refinery facilities but near crude oil production facilities. Information to be recorded includes the status of tanks and separators subject to emission control regulations.

Another aid to the field enforcement officer is the information incorporated in applications to operate the equipment. The permit status of equipment should be routinely checked to detect any changes in equipment or process that might invalidate an existing permit or conflict with variance conditions.

The factors affecting the permit status are (1) change of ownership, (2) change of address, (3) new construction of



TYPES OF CONTAMINANTS			
A		E	
B		F	x
C		G	
D		O	

AREA GRID NO. 8 TFU M.R.NO. 01 -1

FIRM NAME Los Angeles Petroleum Company (XXI) TEL. TA4-2359 ZONE 25

ADDRESS OF PREMISES 12480 S. Oil Road POSTAL ZONE -- CITY Torrance

NATURE OF BUSINESS Petroleum Refining

RESPONSIBLE PERSON TO CONTACT John Doe TITLE Engineer

INSPECTION REPORT

TANK GROUP NO. 4. TANK LIST PREPARED BY George Smith DATE Dec. 11 19 59

Reinspection Record on Back of Sheet

Tank No.	Ht.	Dia.	Type	Gen. Cond.	Product Stored	RVP (lb.)	Prod. Stg. Temp.	Service	Vapor Control	Permit Status	Rules Affected	Remarks
34	29'	30'	C	G	Gasoline	9	ambient	storage	VR	Rule 13	Rule 10, 56	
35	30'	30'	C	G	Stove Oil	negl.	"	"	N	Rule 11-h-5 Rule 13	None	Now off Vapor Recovery
42	12'	60'	C	G	--	--	--	--	N	Rule 13	None	Temporarily out of service
54	30'	40'	C	G	Aviation Gasn.	6	ambient	storage	VR	#10002	Rule 10, 56	
81	51'	110'	F	G	Gasoline	9	"	"	F (SS)	#19163	Rule 10, 56	sl. odors
93	35' 1.	11'	H-P	G	n-Butane	50	"	"	PVV-VR	Rule 11-h-3	None	
142	51'	40'	F	G	Diesel	negl.	"	"	F (SS)	A-19[illegible] Rule 11-h-5	Rule 10	Formerly stored gasoline

Codes and Standard Terminology

Type:	C-Fixed Roof; F-Floating Roof; P-Pressure; O-Open Top; S-Spheroid; H-Horizontal; U-Underground
Cond.:	G-Good; P-Poor; B-Bad
Service:	Rundown; Storage; Blending or Mixing
Control:	N-None; PVV-Conservation Vents; F-Floating Roof (SS-Single Seal; DS-Double Seal); V.R.-Vapor Recovery; V.D.-Vapor Disposal; V.B.-Vapor Balance.

Figure 85. Tank inspection report.

NATURAL GASOLINE, GAS, AND CYCLE PLANT
SURVEY SUMMARY

Company Sunrise Oil Co. of Calif., Inc. +3 Date 3-28-56

Address 1400 Bliss St. City Onyx, Calif.

Phone RA 6-3251

Information by L. M. Black Title Production Engineer

Type of Plant: natural gasoline (x): Absorption ( ), Booster ( ),

Other ( ) Specify: Gasoline plant

Source of material process Wet gas from oil wells

Total No. of wells ____

Throughput: Wet gas 20 mm SCFD: Dry 2 mm SCFD

Natural gasoline (bbl) 475/day Propane (bbl) 0

N-butane (bbl) 0 Butane-propane mixture (bbl) 0

Isobutane (bbl) ____

Boilers: Number 5, Type hrt Heaters: Number 2 Type steam

Type fuel Plant gas Source Plant residue

Quantity of fuel used 400 MCF/day

Is flow diagram available? ____ Can it be obtained? ____

Storage & handling:

Tanks		Oil-Effluent Water Separators	
No. of Tanks	8	No. of separators	1
Vapor recovery	3	No. questionable	None
No. under rule 56	None	Type of control	None
Pressure	4	Floating roof	None
Other (specify)	1 cone roof	No. under rule 59	None
No. controlled	1	No. controlled under rule 59	None
		Totally enclosed	None
		Vapor recovery system	None

Other (specify) None

FEO's remarks re equipment & plant conditions: No leakages.

No losses noted.

FEO J. R. Hardy

Figure 86. Natural gasoline, gas, and cycle plant survey summary.

equipment, and (4) alteration of equipment. The equipment list is constructed to provide reference data which will enable enforcement officers on inventory reinspections to determine whether the permit status has changed. Any untested equipment found in the plant, capable of air pollution will require a permit.

Similarly, alteration of equipment is frequently detected by discrepancies in the equipment description or on the flow chart or by changes noted on engineering applications in the permit file.

(2) Review of safety precautions and procedures - The FEO is accompanied to the unit or units to be inspected by the air pollution representative within the plant or by such other informed refinery personnel as he might indicate.

Personal protection is necessary in many of the industrial locations that an enforcement officer may be required to visit. Safety equipment such as hat, goggles, steel-toed shoes, ear plugs, heavy gloves, gas masks or respirators, and safety flashlights should be available. The field enforcement officer must never enter a plant without the proper safety equipment.

The following is a list of do's and don'ts for field enforcement officers to adhere to during refinery inspections.[12]

1. When entering a plant to make an investigation, do ENTER and leave by the MAIN GATE or GUARD POINT set up by company regulations. Comply with company SECURITY RULES

by registering and wearing a BADGE OF IDENTIFICATION if requested to do so.

2. Do wear a head covering while in a plant, preferably a HARD SAFETY HAT.

3. Do wear RUBBER GLOVES, when necessary, such as when sampling strong acids and alkalies, a RESPIRATOR in an atmosphere of heavy dust or gases, GOGGLES to protect the eyes from caustic solutions, flying particles of steel, sand, and hot oil.

4. In areas containing noxious gases, such as hydrogen sulfide or hydrogen fluoride, a respirator should be worn unless the gas previously has been tested by an MSA DETECTOR and has been found to be below the toxic limit.

5. In the event of FIRE in the area of your inspection, do immediately LEAVE, and remain outside the area until the "ALL OUT" signal is sounded.

6. When inspecting an area where inflammable liquids are being processed, do make certain that there is an avenue of escape before starting the assignment. Look around. If the area appears to be unsafe, leave it until you are assured of its safety by someone in control of the area.

7. When working in an area where strong acid or caustic solutions are handled, do note the location of the nearest water shower for quickly washing off a person accidentally sprayed

with these chemicals.

8. If your clothing becomes sprayed with light oil such as kerosene or gasoline, do change clothing as soon as possible to prevent damage to skin from contact with the oil and to eliminate the hazard of the clothing catching on fire.

9. Do use the buddy system when taking a sample or gauging a tank of volatile or gaseous hydrocarbons. The Field Enforcement Officer should be accompanied by another person and the two persons should remain together until the job is completed.

10. If about to sample a tank, do make certain that all equipment is in workable order before leaving the ground. The uncertain perch atop of a high tank is no place to untangle a line or to force a stubborn bottle in or out of a sampler.

11. Do not smoke or carry "strike anywhere matches" or cigarette lighters which ignite when dropped within an oil refinery. Most plants allow smoking in the main office and certain approved areas with permission of management.

12. Do not open or close VALVES, or start or tamper with any equipment.

13. Do not enter a tank or other confined area where gases may be present unless equipped with a GAS MASK and an ASSISTANT is in attendance outside. Make use of the EXPLOSIMETER to determine the quantity of hydrocarbons present.

14. Do not ascend to the ROOF OF A TANK or other large vessel in the course of an inspection unless accompanied by a company representative, except when you have his permission to proceed alone. Do not step or walk on the roof of a tank unless planks have been laid to distribute the weight of the body, except advised otherwise by the company engineer.

15. Do not poke a flashlight into an open tank hatch or confined area and snap it on. The light may be defective and an explosion might result. It is better to turn the light on away from the hatch and bring it no closer than necessary. Only approved safety flashlights will be used in oil refineries.

16. Do not place the face close to a tank hatch and peer inside to get a better view unless someone is close by to offer assistance in case the gas happens to be toxic.

17. Do not watch a welding torch in action. Failure to observe this precaution could result in painful eye burns.

18. Do not use petroleum distillate or benzol to remove grease from any part of the body unless the action is followed by a thorough rinse with plenty of soap and water. This precaution may prevent a serious case of dermatitis.

19. Do not enter into the immediate area of a flare which might go off at any moment and scorch everything within reach.

b. In-Plant Inspection and Testing - After the preparatory review and paper work have been completed, the FEO undertakes the in-plant inspections.

For gathering evidence in the field, it is useful to include in an inspection kit: binoculars, camera, stop watch, flashlight, maps, compass, smoke tube, and the required forms and regulations.

Cameras are used primarily to photograph excessive emissions from stacks and vehicles and to photograph equipment and operating personnel for identification purposes. Cameras which permit rapid development of photographs at the site of an investigation are especially useful. Moving picture cameras may be desirable for special investigations.

Stopwatches should be of the accumulative type for use in recording total time of excessive emissions within a given period of observations.

The actual techniques which may be used in any given inspection depend upon the specific information to be gathered. For a complex facility such as a refinery, completing the initial inspection may require a number of visits. To optimize the efficiency of the total inspection, individual trip objectives should be planned in advance. Among the inspection techniques which may be useful are:

(1) Sensory observations - Sensory evidence, such as visible discharge and odors disclosed by thorough physical inspection, may be sufficient to determine noncompliance or equipment breakdown in the cases of Ringelmann number readings or excess

hydrocarbon vapor discharge from vapor controlled tankage, for example. However, in other situations, sensory evidence may only be a preliminary or corroborating step to a broader investigation, either because the regulations affected call for evidence not obtainable in this manner (e.g., percentage sulfur in the fuel oil, H_2S grain loading in gaseous products burned and its Btu value, weight of particulate discharge, concentration of SO_2 in discharge of flue gas) or because the control equipment does not discharge a waste effluent directly to the atmosphere. In such cases, the inspector must either rely on data indicating temperature, density, pressure, vacuum or throughput recorded on gages, continuous recorders, high level or density alarms, voltmeters and ammeters, or he must provide for special testing.

Emissions caused by leakage are primarily recognized by sensory evidence. Their detection depends on the ability of the field enforcement officer to recognize odors and trace them to their points of origin. Probable points of origin within refineries include pressure-relief valves, storage vessels, bulk-loading facilities, pump glands, pipeline valves, flanges and blinds, and cooling towers.

The FEO must also note any visible air turbulence caused by light hydrocarbon leakage, frosting of valves or pump glands caused by light hydrocarbon evaporation, liquid leakage, local area discolorations caused by vapor condensate, visible emissions or changes in flow (surging) of an emission, extinguished flare pilot lights or detection of audible gas leaks. These may disclose a violation or a potentially critical situation that should be corrected quickly.

Visible plumes must be noted and their apparent causes recorded for further investigation. Plumes may be caused by incomplete combustion of waste gases in flares, by dust from catalyst regeneration operations, or by breakdowns in various process unit operations.

The field enforcement officer inspecting refineries should thoroughly survey the vapor recovery systems and the facilities for gathering and processing (sour water, wastewater, sour gas, spent caustic, and acid sludge). Even though in a modern refinery most of these streams are treated, their extremely noxious and malodorous characteristics make even the most isolated uncontrolled stream a potential air pollution problem.

Wherever possible, the inspector should point out conditions having a high pollution potential so that the refinery's technical staff may have the opportunity to assess the problem and solve it. More effective use of existing control equipment may be achieved by extending its service to as many uncontrolled sources as is possible without overloading its capacity.

The inspector may find

- isolated streams of sour gas fuel untreated for H_2S removal and recovery
- sour water discharged to open drains with live steam which has not been first deodorized by processing in sour water oxidation or H_2S stripping facilities
- odors and hydrocarbons emitted to the atmosphere from oil-water separators
- malodorous or noxious acid sludge stored in uncontrolled tanks, which release fumes and odors due to breathing and filling losses, or loaded into tank cars and trucks with similar results.

(2) Observing process instrumentation - The process flow charts obtained from plant management in the preparatory phase of the survey should be annotated with operational information relevant to emission evaluation. Operating conditions may be indicated on pressure and temperature gages, manometers, continuous recorders, and other devices. Recording the pressure settings for relief valves can be useful.

(3) On-site testing - At times, the enforcement officer will be called upon to make quick and sometimes crucial, estimates of air pollution problems in any environment. While he cannot make accurate determinations of concentration on the basis of sense perceptions only, he may be able to identify pollutants,

allow for hazardous concentrations, and trace them to a logical source. To eliminate guesswork and to establish identity and concentration within a reasonable degree of accuracy, some field sampling equipment is required. Such equipment, to be of use in enforcement, must be portable, require a minimum amount of bench and field preparation, be of a direct-reading type, yet be substantially accurate. Table 11 lists a variety of contaminants that can be detected or measured by means of simple portable equipment.

Noxious gases, odors, vapors and phenomena for which tests can be made in the field and which require no collection of samples for laboratory analysis are aldehydes, ammonia, aromatic hydrocarbons (benzene, toluene, styrene, xylene) atomic radiation, carbon dioxide, carbon monoxide, chlorine, combustible gases and vapors, organic halides, humidity, hydrogen cyanide, hydrogen sulfide, mercaptans, oxygen (deficiency), and sulfur dioxide.

Certain types of sensitized papers will change color in the presence of physiologically significant concentrations of certain noxious gases, fumes, and dusts. These can be used to test for or to verify the existence of certain suspected contaminants such as ammonia, hydrogen sulfide and phosgene. For example, ammonia reacts with litmus to produce a red to blue color change. Concentrations of ammonia from 0 to 1,000 ppm

Table 11. CONTAMINANTS THAT CAN BE TESTED IN THE FIELD WITH PORTABLE DEVICES

Contaminant	Reason for Testing or Source Test	Reagent or Equipment Used	Treatment or Reaction Observed	Time Required			Concentration Range of Test	Eight-Hour Threshold Limit	Sufficient Warning Without Testing
				a	b	c			
Aldehydes	Eye Irritation Complaints	Absorption in Sodium Bisulfite M. S. A. Midget Impinger	Iodometric Titration	10	5	10	0-1000 ppm	.5 to 5.0 ppm	Yes, Eye Irritation
Ammonia	Odor complaints	Red Litmus & Stop Watch	Color Change to Blue	1	1	0	10- 100 ppm	100 ppm	Yes, Odor
Aromatic Hydrocarbons		M. S. A. Aromatic Hydrocarbon Detector	Colors. Treated Granules. Stain Length						
1. Benzene	" "	" "	Measured	10	2	0	0- 100 ppm	25 ppm	Yes, Odor
2. Toluene	" "	" "	" "	10	2	0	0- 400 ppm	200 ppm	Yes, Odor
3. Xylene	" "	" "	" "	10	2	0	0- 400 ppm	200 ppm	Yes, Odor
4. Styrene	" "	" "	" "	10	2	0	Qualitative	100 ppm	Yes, Odor
Arsine	" " Plating Operations	M. S. A. Arsine Detector	Treated Filter Papers Change Color	10	2	1	0- 100 ppm	0.05 ppm	No
Carbon Dioxide	Exhaust Complaints	Fyrite CO. Analyser	Absorption in Caustic & Measure Vol. Change	1	3	0	0-20%	5000 ppm	No
Carbon Monoxide	Exhaust Complaints	M. S. A. CO Detector	Colors. Treated Granules - Color Change	1	2	2	0-1000 ppm	100 ppm	No
Chlorine	Cylinder Loading & Bleach Mfg.	O. Tolidine in the M. S. A. Midget Impinger	Color Intensity Compared to Standards	10	5	2	0- 70 ppm	1 ppm	Yes, Odor for Immediately Dangerous levels. No, for Low Conc.
Combustible Gases	Venting Storage Tanks Odor Complaints	M. S. A. Model 40 Combustible Gas Indicator	Direct Reading Instrument	1	2	2	0-20 x LEL	---	Some Yes, Odor
Hydrocyanic Acid Gas	Plating Process	M. S. A. Hydrocyanic Acid Gas Detector	Treated Granules Change Color	10	2	0	0- 50 ppm	10 ppm	Yes, Odor, by Trained Personnel
Hydrogen Fluoride	Phosphate Rock	M. S. A. Hydrocyanic Fluoride-in-air Detector	Treated Filter Papers Change Color	5	5	0	.5- 5 ppm	3 ppm	Yes, Odor for Immediately Dangerous levels. No, for Low Conc.
Hydrogen Sulfide	Odor Complaints Refineries & Chemical Processes	M. S. A. H. S. Detector	Treated Granules Change Color	1	2	0	0- 50 ppm	20 ppm	No, Odor is not reliable
Nitrogen Dioxide	Atmospheric	Saltzman Reagent	Color Change Measured	1	1	4	0- 10 ppm	5 ppm	Not reliable
Ozone	Safety Level from Air Purifiers	Rubber Cracking	Time Interval of Cracking Measured	10	20	2	0- 100 ppm	10 pphm	No
Oxygen Deficiency	Closed Vessels or Room	Fyrite Oxygen Analyzer	Absorption Measure Volume Change	5	5	0	0-21%	18-21%	No
Phosgene	Thermal Decomposition of Organic Halides	Treated Filter Papers	Color Change Compared to Standards	5	5	1	1- 100 ppm	1 ppm	No
Phosphine	Mfg. of Acetylene	Treated Granules	Color Stain Length Measured	5	5	2	1- 10 ppm	5 pphm	No
Sulfur Dioxide	Complaints	M.S.A SO detector Treated Granules	Length of Bleaching Action Measured	10	2	0	1- 150 ppm	5 ppm	Yes, Odor
		Reich's Test	Gas Titration	10	10	5	0-1000 ppm		
		Tutweiler	Gas Titration	10	10	5	50 Grains/ft^3		

a. Preparation in Minutes b. Test or Sampling c. Calculation and Interpretation can be detected by this method. Similarly, hydrogen sulfide may be detected with lead acetate, phosgene with diphenylamine, etc.

Another detection system, useful for various contaminants including aromatic hydrocarbons, carbon monoxide, hydrogen cyanide, hydrogen sulfide, and sulfur dioxide uses glass tube ampules containing treated granules which change color when exposed to contaminated air. Air is aspirated through the tubes by rubber squeeze-bulbs, and the length of the discoloration produced is proportional to the concentration of the contaminant.

Combustible gas meters, also called explosimeters, may be used in testing for high concentrations of hydrocarbon gases, vapors, and other combustible gases including carbon monoxide.

More accurate measurements may be made, usually less conveniently, with portable kits for specific chemical tests. Among these are gas-liquid reaction systems such as Tutweiler's apparatus (for H_2S, SO_2, NH_3, and CO_2), Reich's test (for SO_2 by reaction with iodine), and Fyrite analyzers (for CO_2 and O_2).

Midget impingers incorporate a hand-cranked pump to bubble air through impinger tubes for collection of particulate matter or for absorption of soluble gases. For some contaminants, they offer a convenient means of gas-liquid titration, but for other contaminants it is necessary to return the samples to a laboratory for analysis. Fritted glass bubblers may be used in a similar manner, except that insoluble particulates are not conveniently manageable with these devices.

(4) Grab sampling - Where on-site testing is inconvenient or the necessary apparatus for filtering and absorption is unavailable, a simple expedient is to obtain samples for later analysis in the laboratory. "Grab samples" are often obtained by filling gas sampling tubes or inert plastic bags with air by means of motor or hand-powered pumps. The collected air sample is analyzed in the laboratory. For sampling of liquid fuels, as may be required to enforce fuel composition regulations, special containers for flammable liquids are required. Fuel oils of low volatility can be collected in quart or half-gallon tins.

Systems used for the collection of particulate contaminants include sedimentation and settling devices, such as fallout jars and gummed paper stands, miniature cyclone collectors, blower and filter systems, impingers and impactors, electrostatic samplers and thermal precipitators. It is becoming more important to obtain size-discriminating samplers in place of total mass samplers.

The sampling of gaseous contaminants involves separating them from the air in which they are entrained. Such techniques are adapted either to the sampling of specific gaseous compounds or to the determination of gross total concentrations of gaseous contaminants. Specific methods are available for sampling many inorganic gases and some reactive organic compounds. In most cases, these methods involve absorption by bubbling the air through a reactive liquid agent. Mixed gases are usually trapped by adsorption or freeze-out techniques. In any event, an appropriate sampling train must be devised, usually augmented by a suction pump and a wet or dry gas meter.

(5) Source testing - Source tests may be required for a variety of reasons. Among the most critical is the establishment of compliance or noncompliance of the equipment in question with emission standards. Where qualitative estimates are nonconclusive, the field enforcement officer will be the initiator of the test request. The efficiency of the testing operation may depend largely upon the field enforcement officer's adeptness at preparing the test request and his presence during the test to observe the operation of the system under scrutiny. This is especially important in regard to operating parameters that must be maintained as specified during the test.

The request for analysis must state in detail the operating condition of the suspect equipment during the source test. This is necessary so that the appropriate test procedures may be prepared.[13] Basic instructions for the test should include the points to be tested, anticipated contaminants for which the test is run, accessibility of test points (scaffolding), and availability of electric power near the test point. Provisions should be made for portable hoods, or other specialty items where the equipment to be tested does not have an exhaust system. In summary, sufficient data should be made available to the team to avoid surprises during the test. Operating conditions must be defined for the basic system and for the air pollution control system.

- Basic equipment
  - Description of the type, quantity, and rate of material to be processed by the equipment during the test
  - Type, quantity, and rate of usage of fuel
  - Phase of operation during which the source test is to be conducted if the process is not continuous
- Air pollution control system
  - Pressure drop across the control device
  - For scrubbers - water rate
  - For electrostatic precipitators - current and voltage reading, rapping frequency, operating temperature, gas velocity
  - For baghouses - shaking frequency

- Duration and frequency of control device down-time, if any, during the test

The air pollution control system must be in operation during the test. If it is desirable, samples may be taken at the inlet to the air pollution control device as well as the outlet to confirm collection efficiencies.

3. Resurveys and General Surveillance

Because of the complexity of the petroleum industry, unit processes must be inspected systematically and regularly. The frequency of reinspection of any process is based upon the findings during the initial inspection and the recommendations of the FEO and his supervisor. The schedules are printed monthly for each area or special assignment and forwarded to the FEO and his supervisor. The reinspections are scheduled so that they can be completed within a month. The number of reinspections assigned per area is based on the estimate that all required inspections can be completed within one year.

The enforcement officer may have occasion to inspect plants out of schedule because of complaints or violations. In these cases, he does not make a formal inventory reinspection, but uses the copy of the previous inventory record (equipment list), from his files as a check on status of the permit, compliance, or other situation. When a specific air pollution problem is involved, it is best to concentrate on that problem rather than on the inventory of the entire plant. The equipment list can thus be updated during unscheduled inspections.

Vehicle patrol is the principal surveillance method. Field enforcement officers drive their vehicles throughout a defined area - such as a zone, sector, or district - and major traffic arteries to observe evidence of emissions and to detect possible violations of the rules and regulations. The patrol route is laid out to bring the greatest area under view over the shortest distance.

As the enforcement officer becomes familiar with his area, he concentrates on sources requiring the greatest attention and on areas of high source density. He may employ a check list of facilities that are currently involved in permit cases, hearing board actions, recurrent violations, and complaints.

a. Updating the Process Inventory - The process inventory can be used as a tool in gathering evidence. This is especially true in public nuisance cases where it is desirable to eliminate from suspicion all processes or equipment that do not contribute to the nuisance. In such instances, the equipment list serves as a check list.

On an assigned inspection, the enforcement officer must check all equipment units in the plant against those on the equipment list. He is careful to note not only that all equipment listed is identical in important respects, but that they have not been replaced, since a replacement can affect permit regulations. This is usually determined by comparing manufacturer's serial numbers. He also checks for new equipment, alteration of equipment, posting of permits, operation contrary to conditions of permit, etc. Any discrepancies noted are recorded in detail on an inspection report.

Information from the process inventory is input to the permit system data base whenever an enforcement officer prepares or updates an equipment list. The data management system then outputs data from the permit system to schedule inventory inspections and, while doing so, prints out the exact permit descriptions of the equipment.

b. Assessing the Quality of Maintenance - The effective operation of various control systems in a refinery is of basic importance to efficient air pollution control.

Reinspections and surveillance afford the opportunity to observe changes in the condition and performance of control equipment and to detect any development of, or increase in, sources of leakage within a refinery.

Cyclones, electrostatic precipitators and vapor recovery plants are subject to corrosion and other destructive forces which reduce efficiency. In addition, a change in process feed or feed rates due to altered product requirements may also result in overloading or otherwise upset operating conditions in the air pollution control system.

In a vapor recovery system serving tankage, peak loads develop in the morning hours when the heat of the sun produces maximum volumes of hydrocarbon vapors in the space above the liquid. Uneven loading schedules at tank truck loading facilities tend to create a similar situation.

Since a gradual reduction in control efficiency does not always alter the effective operation of the process unit, it may not be noted by operating personnel until a major breakdown occurs accompanied by a serious air pollution situation constituting a public nuisance. It is therefore essential for adequate air pollution control that such areas be inspected regularly and frequently.

Proper design and maintenance of this equipment, together with adequate housekeeping, are required for the efficient control of emissions from refineries and other petroleum industry operations. It is field enforcement officers' responsibility to observe and report, from the physical evidence, the managements' degree of success or failure in this endeavor.

B. ESTIMATION OF LOSSES

Most air pollution control enforcement activity involves investigating compliance with statutory regulations and abatement orders. Regulations include emission prohibitions and performance standards. These standards require that the losses or discharge to the atmosphere of specific contaminants be determined. Inspection of equipment for general emission inventory purposes or for support of permit system activities may also require that losses be estimated.

A variety of direct and indirect techniques, having different levels of accuracy and precision, may be used to estimate losses in petroleum refinery operations. Some direct techniques are source testing and monitoring and physical observation. Indirect techniques employ material balance, related process variables, perimeter monitoring, and emission factors.

1. Direct Estimation Techniques

a. Source Testing and Monitoring - When performance or emission standards are given in allowable mass rates of discharge or concentrations, source testing or monitoring is normally used to achieve the accuracy required for enforcement. This does not mean that a reasonable estimate of losses cannot be made for a specific source when a previous correlation has been developed between an observation and actual test data.

Source testing differs from source monitoring in that the former is limited in scope to a specified amount of time while the latter is continuous. Also, samples extracted for source testing are examined or analyzed elsewhere while samples extracted for source monitoring are examined in situ. The field enforcement officer in a large diversified control agency normally would not participate in source testing except as an observer of the process or of visual emissions. In a smaller organization, and depending upon his qualifications, the FEO may also participate in the actual test operations. In both situations, the field enforcement officer will be expected to initiate requests for source testing when he has reason to believe that a violation of a regulation exists.

Readings from source monitoring instruments which the field enforcement officer may take during on-site inspections can be used to estimate losses although nomograms or further calculations may be required to convert the instrument readings to useful emission terms. Most of the source monitoring instruments normally used in a refinery (see Chapter IV) measure concentrations of contaminants. If performance standards are given in terms of mass flow rates, the FEO must be able to estimate the loss rate in those terms. Suppose, for example, that the emission standard was given in terms of pounds of particulate matter lost per pound of material processed, and the analyzer was calibrated in terms of lbs./ft.^{3} (at stack conditions), then

$$E = \frac{CQ}{W_p}$$

where

E = emissions, $\frac{\text{lb. contaminant}}{\text{lb. process weight}}$

C = concentration, $\frac{\text{lb. contaminant}^*}{\text{ft.}^3\text{ stack gas}}$

Q = stack gas flow rate, $\frac{\text{ft.}^3}{\text{hr.}}{}^*$

W_p = process weight, $\frac{\text{lb.}}{\text{hr.}}$

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* Both C and Q at the same stack conditions or corrected to standard temperature and pressure.

If an instrument does not measure in the units required, then a calibration chart will be needed to convert to the proper units.

b. Direct Observation - The field enforcement officer uses his powers of direct observation of an effluent stream to estimate losses at many points. The most common example is in determining the Ringelmann Number of black smoke or the equivalent opacity of any visible plume. Also included would be observation of liquid hydrocarbon leaks from pump seals, flanges, and relief valves and from blind changing. It could include estimation of losses from flare operation, from conditions in oil-water separators, from odor intensity inside plant boundaries, and from fugitive dust (that is, dust from open storage of bulk materials, from uncovered materials-handling equipment, and from unpaved roads and exposed soil).

Training is the key to achieving an acceptable level of proficiency in using observational estimation techniques. This requires the repetitive making of estimates which are verified by an objective measurement procedure at the time of observation. Opacity observations, for example, are accepted in court. When carried out by a trained observer under correct conditions, procedures for making visual opacity determinations are to be found in the Field Operations and Enforcement Manual for Air Pollution Control[14] and in the EPA Standards of Performance for new Stationary Sources.[15]

2. Indirect Estimation Techniques

a. **Data from Process Instruments** - Process instruments are used to secure efficient and safe operation of the various process units in a refinery. Where the parameter being measured is closely related to the potential for effluent losses or to the efficiency of control equipment, the process instrument is a useful tool in the estimation of losses.

Most process instruments are used to measure flow, pressure, and temperature. Normally, a measurement per se may not permit the estimation of losses. However, any evidence of unstable or off-limits operation may give an indication that excessive demands are being placed upon control equipment and that losses may increase as a result.

There are many situations in which pressure, flow, or pressure/vacuum measurements may aid in the estimation of losses or potential for losses. First, the temperature and flow rate of gas entering a carbon monoxide afterburner (CO boiler) serving a fluid catalytic cracker catalyst regenerator unit will indicate whether there is sufficient residence time and a high enough temperature for the complete conversion of carbon monoxide to carbon dioxide to take place. Minimum temperature and residence times may be specified by permit conditions and are provided for in the new source performance regulations of the EPA for fluid catalytic cracking units in petroleum refineries.[15]

Though not routine, flow rate monitoring for waste gas or emergency flares will yield data that may be used to estimate losses if the composition of flare gases is known.

Vacuum recording at vapor recovery systems can give an indication of the adequacy of compressor and recovery system capacity. Where insufficient capacity results in other types of venting or flaring, estimates of the losses can be made.

Voltage measurements on electrical precipitators can be used to estimate some of the performance characteristics of such control equipment although specific knowledge of the design specifications of the equipment would be necessary to interpret this data.

Pressure drop measurements across cloth filter units are valuable in estimating the degree of bleed-through, whether capacity is being exceeded, whether the cleaning cycle is adequate, and in some cases, whether bags are ruptured. Again, specific knowledge of the design pressure drop is necessary to interpret these findings.

Absorber solution circulation rates and indications of strength such as pH are process measurements that may be useful in estimating effluent losses in acid gas scrubbers or absorbers. Because of the high dependence of scrubber performance on these parameters, very good estimates may be possible.

The collection efficiency of almost all air pollution control equipment decreases with an increase in the effluent gas flow rate. A possible exception is the centrifugal collector class, but increased flow in these devices results in such high pressure drops that capacity is somewhat self-limiting. Therefore, as a general case, effluent gas flow rates in excess of design capacity can be expected to increase losses both by virtue of the increased flow and the loss in collection efficiency as well.

A very special case of process monitoring involves the analysis of fuel oil and fuel gases for sulfur content. This is particularly applicable to the sulfur content of refinery "make gases". These are gases that result from refinery operations. They have a reasonably high heating value and are used as supplementary fuel for heaters rather than being further processed. Sulfur content information so obtained, together with usage rates, can be used directly to calculate sulfur losses to atmospheres.

b. Equipment Inspection and Operational Data - Estimates of contaminant losses may sometimes be made by observation of operating techniques, by inspection of equipment condition, by determining level and adequacy of maintenance, and by evaluation of process data not determined analytically.

Hydrocarbon losses from storage tanks vary with color and condition of paint, with product throughput, with vapor pressure of product and, in the case of floating roof tanks, with the condition of seals and interior surface. Specific calculation procedures for determining losses from storage tanks have been reported elsewhere[8] and are not normally applied in the field. However, the field enforcement officer should be aware of the influence of these factors so that estimates can be made of the potential influence of changes in them. The conditions and proper functioning of floating roof seals is, for example, very important in maintaining losses at the expected levels.

The field enforcement officer must learn the kind and frequency of maintenance necessary to keep control equipment in effective operating condition. For example, fluid catalytic cracker dust is sufficiently abrasive to wear through the high efficiency cyclones generally used as collection equipment in front of an electrostatic precipitator. If excessive wear results in high dust loadings to the precipitator, losses to atmosphere will increase.

Losses would also be expected to increase as a result of inadequate maintenance of relief valves and pump seals although in these situations visible emissions may also increase. Electrostatic precipitators, cloth filters, and mist eliminators also require regular maintenance. The principal maintenance problems with electrostatic precipitators are related to the power supply, particularly voltage level and regulation. Broken electrodes must be replaced, collection plates and tubes must be kept in the proper condition, alignment must be maintained, and rapping mechanisms must operate properly.

Fabric filters require regular inspection and replacement of bags. Based upon the fabric used, the severity of service, and the cleaning procedure, an estimation can be made of expected bag life. Bags must, of course, be mounted properly to avoid overstressing the fabric and to preclude leaks at points of fastening. The bag cleaning mechanism whether involving shaking, rapping, or reverse flow must be maintained. Timers, solenoid valves, and mechanisms, all require maintenance and are subject to failure.

Mist eliminators, such as those used on sulfuric acid plants and on the discharge of some absorption columns, are passive devices and somewhat less subject to failure than the other equipment. In some cases, however, depending upon the materials used and the severity of service, corrosion or clogging may occur which will disrupt design flow patterns or reduce collection efficiency. Sagging or compression of the eliminator media (usually metal or glass fiber mesh) may also result in loss of efficiency.

Operational data that does not appear on process instruments may also give an indication of possible emission losses.

Examples would include catalyst make-up rates, change in nature of materials being processed, and operator comments in shift logs.

c. Data from Air Sampling Equipment - Information available to the field enforcement officer from ambient sampling which might be of use in assessing losses will for the most part be obtained by the use of portable or hand-held sampling equipment or by perimeter monitoring equipment. The portable or hand-held devices are most likely to be useful inside or close to the plant boundary, although under unusual conditions they may be used to verify outside complaints. Sampling would be conducted regularly at a series of points within and near the refinery boundary. These points would be selected on the basis of past experience, proximity to known sources, and subjective criteria such as location where certain odors have been or are detected.

Sampling devices or indicator tubes are available to measure hydrogen sulfide, sulfur dioxide, carbon monoxide, ammonia, mercaptans, phenols, and hydrocarbons. These measurements are useful mainly in a qualitative sense because of limitations in accuracy, specificity, and knowledge of the amount of dilution of the contaminants after discharge from the source. That is to say they are most useful in identifying unusual loss or emission conditions which may be related to leaks or operational malfunctions.

Perimeter monitoring as used here means formalized monitoring at sites established outside the refinery boundaries. Contaminants monitored at these sites would most likely be those identified as being of major importance, either because of actual or potential volume of release, toxicity, or impact on meeting air quality standards. Expected values for the contaminants monitored, based upon known release rates and meteorological conditions, through use of diffusion modeling should be determined. Then a normal pattern should be established, which the field enforcement officer should be able to use to estimate changes in source strength through observation of the recorded contaminant concentrations.

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VII. MAINTENANCE

A. DESCRIPTION OF REFINERY MAINTENANCE OPERATIONS

Maintenance is a major activity at all refineries. A large portion of the work force is assigned to maintenance operations. These operations can be categorized as routine or emergency. Emergency maintenance is required to clean and repair facilities damaged by accident. Emergencies such as ruptured lines, fires, and explosions must be considered from the safety standpoint first and from the pollution standpoint second. Other emergencies, such as a broken compressor shaft, can be handled with more attention to pollution control.

Routine maintenance can be categorized as minor or major. Minor maintenance includes the day-to-day upkeep of individual equipment items. Major maintenance involves the shutdown and repair of entire processing units or even the entire refinery. These "major turnarounds" are performed on a regular basis, usually at intervals of two or three years. Routine maintenance is carefully scheduled and planned whether it is minor servicing of equipment or a major refinery turnaround.

Record keeping is an essential part of a refinery maintenance program. Maintenance records are kept primarily to facilitate planning and work schedules. In some large refineries, electronic data processing equipment is used to improve the efficiency of maintenance operations. Maintenance records are useful to determine the state of repair of individual pieces of equipment. These records can, therefore, be used to review the maintenance history of equipment items known to be pollution sources. Emission control equipment with histories of frequent upsets and malfunctions can often be detected easily by reviewing the maintenance records before beginning the field inspection.

B. GENERAL PLANT MAINTENANCE

Routine maintenance operations within the refinery may contribute to air pollution. Major turnarounds are often handled by contractors who specialize in refinery maintenance. The procedure in a major shutdown will vary widely depending on the individual refiner's practices. In most cases, all liquid material is pumped to product and intermediate storage or slops tanks. As the plant is depressurized, gases are delivered to the blowdown system.

If acid gases are present, these can be delivered to the fuel-gas system or the acid-gas recovery unit. Tanks and vessels are steamed out to remove toxic and flammable gases. Generally, the steam vapors are vented to the atmosphere and pollutants escape.

The vapors can, however, be vented through a condenser to a flare where such an arrangement is justified. The shutdown procedure followed in each case will greatly affect the quantity of air pollutants emitted. At present, complete recovery of air pollutants during shutdown is not practiced. Ventilation of vessels and tanks is required for safety reasons during repair. Noticeable odors are generally unavoidable at these locations.

The repair and cleanup operations represent a source of air pollution during both major turnarounds and day-to-day operations. Tanks, vessels, and towers require sandblasting and painting. Sandblasting can be the source of particulate air pollution resulting in property damage or health hazard. In some cases, protective tarpaulins or wet blasting can be used to reduce dust emissions. Smaller items can be removed to remote sandblast facilities equipped with dust collectors. The use of steel shot or grit can also be used in place of sand. Paint spraying results in particulate and hydrocarbon emissions. Nonreactive paints and solvents should be used. Outdoor paint spraying is illegal in some areas. Solvent cleaning may also be a source of air pollution. Nonreactive solvents should be used.

C. MAINTENANCE OF AIR POLLUTION CONTROL EQUIPMENT

1. Flare and Blowdown System

A blowdown system consists of relief valves, blowdown piping, liquid knock-out drum, and flare stack. The operation of a blowdown system is discussed in Chapter I, Section U. Relief valves are discussed in Chapter II, Section H. The blowdown system is designed primarily as an emergency shutdown system. The proper operation of the system, however, is essential to the reduction of air pollution from relief valves and flare stacks.

Relief valves are normally removed from service and are shop repaired on a regular basis. Relief valves should be tested for correct operation at regular intervals. If this is not possible, spare valves should be installed to permit removal and servicing. Service records can be reviewed to determine the inspection frequency. It is essential that the valves be clearly marked and replaced in the proper location. Tank vents and flame arresters also require regular inspection to assure proper operation.

The flare stack is designed to operate under a wide range of conditions. Since materials of wide ranging properties are processed by the blowdown system, plugging of lines is a possibility. Blowdown lines and knock-out vessels should be regularly inspected to maintain them free and clear. Control systems on the liquid knock-out drum must operate properly to prevent flooding of the flare stack. The gas pilot equipment and purge gas lines must be in good operating condition if the blowdown material is to be combusted completely.

2. Particulate Matter Control Equipment

Particulate matter is controlled in refineries through the use of cyclone separators, electrostatic precipitators, and - to a lesser extent - baghouses. Cyclone separators can plug at the dust outlet if viscous material is introduced. Pressure buildup should be monitored to determine if the cyclone is operating as designed.

Electrostatic precipitators are used to recover catalyst fines in some refineries. These units can malfunction if tars or other materials foul the collection plates. Regular inspection and cleaning is required. Ionizer wires will corrode and require replacement. Electrical control systems require checking to assure the proper voltage and rapping frequency and intensity. Operating conditions may have to be adjusted if particulate properties vary with time.

Baghouse filters require regular maintenance to ensure efficient operation. This includes regular removal of the collected dust, inspection of the bags, and lubrication of the moving parts. If required, the bags should be replaced. Precoating of bags after each cleaning cycle with dust is recommended to improve collection efficiency, but may not be required in all cases.

3. Sulfur Recovery Plants

Sulfur recovery plants are an important source of sulfur dioxide pollution in refineries. An upset can result in sharply increased emission rates. The operation of sulfur plants is discussed in detail in Chapter I, Section P. A sulfur plant generally requires little attention. Proper operation of the inlet mixture control valves is essential to complete conversion of sulfur compounds to elemental sulfur. Sudden surges in feed rate or composition can also upset the performance of the plant. Frequent inspection is required to determine catalyst activity. The tail-gas incinerator must be inspected for corrosion. Air/fuel mixture control instruments should be inspected. Since a sulfur recovery plant is processing a poisonous gas, alarm systems are provided to announce plant upsets.

D. MAINTENANCE OF MONITORING EQUIPMENT

A wide variety of monitoring equipment is available. Sampling devices and analytical instruments are commercially available. Manufacturers' instructions should be carefully followed for use and maintenance of monitoring equipment. Portable instruments can be easily damaged in transit. Instruments located outdoors can be damaged by the elements. Attempts to use equipment under conditions other than those intended by the manufacturer may also cause damage. Titrating solutions should be sealed tightly when not in use. Fresh solutions should be used and frequently checked for concentration. Regular calibration and inspection of instruments is essential. A maintenance record should be maintained on each monitoring device.

VIII. PERSONNEL

A. MANPOWER REQUIREMENTS

Of the field and enforcement functions performed by air pollution control agencies, those relating to petroleum refineries and to the petrochemical and chemical industries are probably the most specialized. Since these industries are likely to constitute large point sources of pollution, as well as the cause of public complaints, an organizational component within the agency (or at the very least, special assignments) should be dedicated to the surveillance of these industries. The manpower and the degree of specialization required will depend on the number and types of such installations located within the jurisdiction of the air pollution control agency.

Few air quality control regions contain a sufficient number of petroleum refineries to justify a special operating unit. In most cases, petroleum refineries are grouped with other plants requiring chemical engineering expertise and with activities related to the petroleum economy of the area.[1,2] These include:

Asphalt manufacturing plants

Chemical plants, including manufacturers
  of sulfuric acid, vinyl chloride, paint
  and varnish, and fertilizer
Gasoline absorption plants
Natural gas processing plants
Oil reclaiming plants
Petrochemical plants
Petroleum marketing and consumption
Petroleum marketing stations, service
  stations, bulk plants, marine terminals
Soap and detergent manufacturing plants
Sulfur recovery plants
Tank farms

With a few exceptions (such as power plants and ships), these industries are organized from unit processes - those involving a chemical change in one or more reactants (e.g., nitration, polymerization, hydrogenation) - and unit operations - those involving physical changes only (e.g., distillation, absorption). Both unit processes and operations may be defined in terms of the process unit, that is, the equipment or process vessels interrelated by flow systems in which materials are progressively transformed towards a desired end.

Surveillance work levels tend to be related to the number of process units with significant air pollution potentials rather than to the number of industrial plant address-locations. On the average, a process unit in this industry may require three hours of surveillance and inspection time. This includes surveillance, equipment inspection, plant personnel interviews, and report write-up, exclusive of detailed engineering evaluation, permit processing, and court and hearing board activities. At an inspection frequency of four times per year, 12 man-hours of field time per year per process unit would be required. Thus about 160 process units is equivalent to one man-year of surveillance for the industry. This would be equivalent to eight petroleum refineries each averaging 20 process units that are significant from an air pollution standpoint.

Of course, these averages will vary among agencies, depending on the personnel available and delegation of responsibilities. Field personnel who are also responsible for permit evaluation (as opposed to a separate permit processing unit) or for source testing will require significantly more man-hours per process unit. Ideally, for maximum efficiency, permit and source testing operations should be separated from surveillance operations. A grouping of installations in terms of process/work units and in terms of the types of surveillance and enforcement functions required will help to determine the manpower, organizational structure, and support services that will be needed.

B. FEO FUNCTIONS

The functions of the field enforcement officer to be performed in connection with petroleum refineries are discussed in Chapter V, "Maintenance of Refinery Records" and Chapter VI, "Estimating and Assessing Emissions". To summarize, these functions are:

1. Maintain surveillances of all process, equipment, and activities associated with assigned petroleum, petrochemical, or chemical installations, by means of vehicle patrol or other exterior procedures. The purpose of this surveillance is to detect visible emissions, odors, new construction, or other obvious changes in plant conditions which may affect emission rates or permit status.
2. Conduct surveys and inspections of all processes, equipment, and activities that have air pollution potential to establish, at each and every definable source of pollution, compliance or noncompliance with all rules and regulations.
3. Investigate all citizen complaints made in connection with these installations.

To perform these duties, certain capabilities are required of the air pollution control agency, the enforcement operation, and the individual officers.

The air pollution control agency and, desirably, the field enforcement operation should have personnel with baccalaureate degrees in chemical engineering and previous work experience in the industry. Even with such training and experience, personnel should receive as much as 100 hours of formal on-the-job training. Training should include courses in petroleum technology, and air pollution engineering and enforcement. Courses may be available from a nearby university or from the EPA or they may be created and implemented by the air pollution control agency itself.

The specialized personnel should be available to perform such functions as permit evaluation, plan review, engineering supervision, supervision of specialized enforcement activities, technical services, and general agency planning and evaluation. In any event, the field enforcement operation should either be supervised by, or have access to, these personnel. In larger agencies, particularly agencies responsible for large petroleum, petrochemical, and chemical plant complexes, highly trained and experienced personnel should occupy senior field enforcement positions.

C. FEO PERSONNEL QUALIFICATIONS

If the expertise described above is directly available to the enforcement operation, then it is not necessary for FEOs to possess degrees and previous experience in chemical engineering. Using such personnel in the field may be inefficient, since not all of the engineering capabilities of such persons would be needed in the field operations program.

The qualifications of field enforcement personnel should be looked upon, primarily, in terms of aptitude, including ability to receive special-purpose training and, secondarily, in terms of general education and previous work experience.[3] With respect to aptitudes, FEOs should be able to:

1. Assimilate and comprehend (1) engineering information related to chemical and physical processes and (2) legal and administrative information related to enforcement activities;

2. Recognize equipment, process configurations, and operating conditions or parameters (particularly pressure and temperature) that affect air pollution emissions;

3. Relate equipment, processes and conditions to specific processing functions (unit processes or operations) and to the specific substances (input and output) involved in such operations;

4. Identify abnormal operating conditions, e.g., process upsets, overloads, breakdowns, equipment failures;

5. Become familiar with the chemicals and materials employed, particularly hazardous substances, and understand the technology and terminology of the industry;

6. Evaluate visible and nonvisible emissions, including odors, and materials-damaging substances;

7. Prepare and interpret process flow data and make preliminary estimates of material losses; and

8. Prepare concise, accurate, and complete reports which effectively communicate the technical information necessary to

establish compliance or noncompliance of specific sources with the rules and regulations.

These personnel aptitudes or capabilities can be determined from:

1. General intelligence tests. Candidates should have high verbal and arithmetical scores, including reading comprehension and vocabulary skills.

2. Scholastic records and courses pursued in high school, junior college, college, and technical institutes with respect to exposure and performance in technical and scientific courses.

3. Previous work and military experience, especially in technical areas and responsibility and level of contact with public (e.g. engineering sales activities).

4. Special aptitude tests. These can be developed and used to identify and select potential FEO candidates. Skills and aptitudes that can be evaluated include interpretation of flow charts, comprehension of technical information with respect to chemistry, heat transfer, principles of conservation of energy and mass and fluid flow. Personality tests can be used to help assess judgment, emotional stability, ethics, and responsibility.

5. The degree of motivation. Motivation is a very important factor, since FEOs generally operate in the field under minimal supervision and are responsible for planning and scheduling much of their own work. In effect, they are responsible for the installations

they are assigned to, and it is up to them to conduct all necessary research and collect all information they may need to understand the operations of these installations.

6. Approach and appearance. Neatness, maturity, objectivity, and responsibility are essential qualities in relating to operating personnel at all levels.

D. TRAINING

Personnel meeting these qualifications should receive at least 100 hours of classroom and on-the-job training. They also must work under supervision of experienced field personnel prior to entering and inspecting petroleum refineries on their own. Courses should include:

Air Pollution Control Technology
Care and Use of Inspection Equipment
Drivers Training
Field Orientation
Legal Authority
Monitoring Instrumentation
On-the-Spot Field Testing
Petroleum and Petrochemical Technology
Report and Notice Writing
Smoke School
Supervised Field Training

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GLOSSARY

A

ABSORPTION: A process whereby a liquid dissolves a gas, such as oil which absorbs light hydrocarbons from natural gas.

ABSORPTION GASOLINE: Gasoline which is obtained from natural gas by absorption in oil.

ACCUMULATOR: A vessel which serves as a surge tank and holds intermediate product, usually overhead distillate.

ACID GAS: A gas consisting mostly of hydrogen sulfide and carbon dioxide.

ACID TREATING: A process in which petroleum products are contacted with sulfuric acid.

ACTIVATED CARBON: A form of carbon or charcoal which has a high adsorptive capacity for gases, vapors or solids.

ADDITIVES: Chemicals added to petroleum products to improve performance or obtain needed product characteristics.

ADSORPTION: A process in which a gas or vapor physically adheres to the surface of a solid such as activated carbon.

AEROSOL: A continuous dispersion of solids and liquids in a gas, usually air, such as a haze or fog.

AIR BLOWING: A process in which hot asphalt is oxidized by passing air through it.

ALIPHATIC HYDROCARBONS: Open chain hydrocarbons such as paraffins and olefins.

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ALKYLATION: A process for combining isoparaffins and olefins such as isobutane and butylene, to form alkylate, a gasoline component.

AMINE UNIT: A process in which acid gases are removed from hydrocarbon gases by absorption in amine solution.

ANILINE POINT: An index for measuring the solvent capacity or aromatic content of hydrocarbons.

ANTI-KNOCK COMPOUNDS: An additive in gasoline, such as tetraethyl lead, for improving combustion characteristics in internal combustion engines.

API: American Petroleum Institute.

API GRAVITY: An index for measuring the density of petroleum.

API SEPARATOR: A device for separating oil from water by gravity.

AROMATIC HYDROCARBONS: Hydrocarbons with an unsaturated closed ring structure, such as benzene, toluene and xylene.

ASH: A nonvolative, incombustible component of fuels which remains after combustion.

ASPHALT: A high, boiling, semi-solid hydrocarbon refined from crude oil. A component of asphaltic-base crude oils.

ASTM: American Society for Testing Materials.

AVIATION GASOLINE: A grade of gasoline for reciprocating aircraft engines.

AZEOTROPIC DISTILLATION: A process for separating hydrocarbons of the same boiling point.

B

BARREL: A volume unit used in the petroleum industry consisting of 42 U.S. standard gallons.

BENZENE: An aromatic hydrocarbon present in some crude oils.

BFW: Boiler feed water.

BITUMEN: See Asphalt.

BLACK OIL: Petroleum containing residual crude oil.

BLOWDOWN: Material purged from the refining process during startups, shutdowns, and pressure relieving. The blowdown system collects and disposes of the waste material.

BS&W: Bottom settlings and water material found in tank bottoms.

BTU: British thermal unit - used to define heating value of fuels. The heat required to raise one pound of water one degree Fahrenheit.

BUNKER FUEL OIL: A heavy residual fuel oil.

BURNING OIL: See Kerosene.

C

CALCINED COKE: See Coke.

CASINGHEAD GASOLINE: See Natural Gasoline.

CATALYST: A substance used to accelerate chemical reactions.

CAUSTIC: A term used for solutions of sodium hydroxide used in treating processes.

CETANE: A paraffin used as a standard for diesel fuel quality.

CLAUS PROCESS: A process in which hydrogen sulfide is converted to elemental sulfur.

COKE: Solid carbonaceous residue obtained from coking residual crude oil. Calcined coke is coke that has been heat treated to remove volatile materials.

COKING: A process in which crude oil is destructively distilled to produce petroleum coke.

CONDENSATE: A liquified hydrocarbon gas such as obtained from natural gas wells.

CONVERTER: See Shift Converter.

CRACKED GASOLINE: Gasoline obtained by cracking heavier petroleum fractions.

CRACKING: A process in which large hydrocarbon molecules are divided into smaller molecules. Process may be catalytic or thermal cracking.

CUTBACK: Petroleum fractions used to reduce viscosity of fuel oils and asphalt.

CYCLE STOCK: Intermediate refinery product which is recycled to other process units.

D

DEA: Diethanolamine, an absorbent used to remove acid gases for sour gas streams.

DEAERATOR: A device used to remove dissolved oxygens from boiler feed water.

DEASPHALTING: A process in which asphalt is removed from reduced crude.

DEBUTANIZER: See De-ethanizer.

DE-ETHANIZER: A distillation column which removes ethane and lighter hydrocarbons from propane and heavier hydrocarbons. The terms depropanizer and debutanizer are also used for similar operations.

DEHYDRATING: A process in which water is removed from hydrocarbon gases and liquids.

DEPROPANIZER: See De-ethanizer.

DESALTING: A process in which salts are removed from crude oil.

DEWAXING: A process in which wax is removed from lubricating oils.

DIESEL FUEL: A petroleum product used as fuel in diesel engines consisting of gas oils.

DISTILLATE: The light material taken overhead in a distillation column and condensed.

DISTILLATION: A process in which a. hydrocarbon feed is separated in two or more components of different boiling points.

DOCTOR TEST: A test used to determine the mercaptan content or odors of petroleum products. Odor-free products are termed "Doctor Sweet".

DRUM: A container which holds 55 gallons. Also, a vessel used in the refinery process for storage or separation.

DRY GAS: A hydrocarbon gas, usually natural gas, which does not condense easily. Usually contains mostly light hydrocarbons, such as methane and ethane.

E

ENTRAINMENT: Liquid droplets or mist contained in vapors leaving a boiling liquid.

EXTRACTIVE DISTILLATION: A distillation process in which hydrocarbons with similar boiling points are separated by selective absorption in a solvent.

F

FLARE: A device used for burning waste gases. See Blowdown.

FLASH DRUM: A vessel used to separate vapors and liquids after a pressure reduction.

FLASH POINT: The minimum temperature at which vapors above a petroleum fraction or product will ignite in the presence of a flame.

FLOATING ROOF: A roof which floats on surface of liquid in a storage tank and reduces evaporation losses.

FRACTIONATOR: See Distillation.

FUEL GAS: Light hydrocarbon gases generated in the refinery process used for firing process heaters and furnace.

FURFURAL: An organic compound used as a solvent in refining lube oils.

FURNACE OIL: Distillate fuel oils used for residential and commercial heating.

G

GAS OIL: A fraction obtained in the distillation of petroleum generally used in distillate fuel oil.

GASOLINE: Refined petroleum naphtha used in internal combustion reciprocating engines.

GRAVITY: See API Gravity.

H

HEATING OILS: See Furnace Oils.

HOT CARBONATE: A potassium carbonate solution used to absorb acid gases from light hydrocarbon streams.

HYDRODESULFURIZING: A process in which sulfur is removed from petroleum in the presence of a catalyst by combining the sulfur with hydrogen.

HYDROTREATING: A process in which petroleum is reacted with hydrogen in the presence of a catalyst to remove sulfur or to hydrogenate unsaturated compounds.

I

ILLUMINATING OIL: See Kerosene.

ISOMERIZATION: A process in which normal hydrocarbons are converted to isomers by rearranging the molecular structure. A typical isomerization is the conversion of butane to isobutane.

J

JET FUEL: A kerosene based fuel for use in gas turbine powered aircraft. JP-4 and JP-5 are common grades of jet fuel.

K

KEROSENE: A petroleum distillate boiling between naphtha and gas oil. Used in jet fuels and heating oils.

KNOCK: A property of gasoline related to octane rating and engine knocking.

KNOCKOUT DRUM: A process vessel used to remove entrained liquid from gases.

L

LPG: Liquified petroleum gas. A petroleum product containing propane and butane.

LAMP OIL: See Kerosene.

LEAD: Refers normally to lead additives in gasoline, such as tetraethyl lead.

LEAN OIL: An absorption oil which contains no dissolved light hydrocarbons.

LIGHT: A relative term applied to petroleum fractions to denote the lower boiling material, such as light naphtha, light gas oil.

LIGHT ENDS: Light liquid hydrocarbons, typically ethane, propane and butane.

LOADING RACK: A structure used to load petroleum products into tank trucks, rail tank cars or barges.

LONG RESID: Residual oil obtained from crude distillation containing neutral oils.

LUBE OILS: A petroleum fraction, generally heavy gas oils, vacuum gas oils and neutral oils used for lubricating purposes.

M

MEA: Monoethanolamine, an absorbent used to remove acid gases from sour gas streams.

MERCAPTAN: An organic compound present in "sour" crude oil. Mercaptan compounds contain sulfur and have a strong odor.

METHANATION: A process in which carbon monoxide is converted to methane by reaction with hydrogen.

MOTOR OILS: See Lube Oils.

MOTOR SPIRIT: See Gasoline.

N

NAPHTHA: A petroleum fraction boiling in the gasoline range.

NAPHTHENES: A group of hydrocarbons having a saturated ring structure such as cyclohexane found in naphthenic crude oils.

NAPHTHENIC ACID: A corrosive organic acid found in some naphthenic crude oils.

NATURAL GAS: Light hydrocarbon gases naturally formed in the earth. May also refer to the finished product or pipeline gas.

NATURAL GASOLINE: A mixture of light hydrocarbons boiling in the gasoline range recovered from natural gas.

NEUTRAL OILS: Distillate petroleum fractions, generally heavy gas oils, having specific viscosity properties and used in lube oils.

O

OCTANE NUMBER: An index used to measure the anti-knock properties of gasoline. Research, Motor and Road Octane Numbers are three different octane ratings.

ODORANT: A material added to fuel gas to impart a distinctive odor and permit human detection.

OLEFINS: A class of paraffin hydrocarbons which are "unsaturated" or deficient in hydrogen, such as ethylene, butylene.

ON STREAM: A term to denote that a refinery or process unit is in normal operation.

OVERHEAD: The vapors which are boiled off the top of a distillation tower or the lightest product obtained in the distillation process.

P

PALE OIL: A distillate lube oil, yellow in color.

PARAFFIN: A series of linear and branched hydrocarbons fully saturated in hydrogen, such as methane, propane. Also known as alkanes. High molecular weight paraffin in solid form is known as paraffin wax.

PETROCHEMICAL: A chemical compound, intermediate or product derived from natural gas or crude oil.

PETROLATUM: A semisolid product obtained by filtration containing residual oils and wax.

PETROLEUM COKE: Coke derived from crude oil. See Coke.

PETROLEUM SPIRITS: A distillate product used in solvents, varnishes and paint thinners.

PHENOL: An organic chemical used in solvent extraction processes.

PHOTOCHEMICAL REACTION: The process of chemical change in the presence of radiation, such as the reaction of hydrocarbons in sunlight to form smog.

PIPELINE GAS: Refined natural gas sold to residential, commercial and industrial customers.

PLUME: The path taken by visible discharges from a stack or chimney.

POLYMER GASOLINE: A gasoline component obtained by combining two olefins.

POLYMERIZATION: A process in which two or more molecules are combined. Typically, refers to the combination of two olefins, such as propylene and butylene, to form polymer gasoline.

POUR POINT: The minimum temperature at which a petroleum fraction will flow.

PRESSED DISTILLATE: The oil obtained when wax is separated from paraffin distillates.

PRESSURE DISTILLATE: Distillate obtained from cracking stills.

Q

QUENCH: The process of cooling hot gases or liquids by direct contact with cold liquid. Usually refers to quench tower or quench oil.

R

RAFFINATE: That portion of the oil which is not absorbed by the solvent in the solvent refining process.

RANGE OIL: See Kerosene.

RAW GASOLINE: See Wild Gas.

REBOILER: A heat exchanger used to boil liquid to provide vapors to the bottom of a distillation column.

RED OIL: A lube oil which is red in color.

REDUCED CRUDE: The crude oil remaining after distillate products have been removed in the crude distillation process.

REDWOOD VISCOSITY: A measure of viscosity used in the petroleum industry.

REFLUX: That portion of the overhead vapors that is condensed and returned to the distillation column.

REFORMING: A process in which the octane rating of naphtha is increased by catalytic reaction or mild thermal cracking. The reformed product is termed reformate.

REID VAPOR PRESSURE TEST: A standard test used to measure the vapor pressure of gasoline and other petroleum products.

RESIDUAL FUEL OIL: Fuel oils containing reduced crude.

RICH OIL: An absorption oil containing dissolved hydrocarbons.

S

SAYBOLT-FUROL, SAYBOLT-UNIVERSAL: Measures of viscosity used in petroleum industry.

SCALE WAX: Wax obtained by sweating the oil obtained from slack wax, that is separating excess oil from oily wax.

SEDIMENT: See BS&W.

SHIFT CONVERTER: A reactor used to convert two compounds to two different compounds, such as are used in sulfur plants and hydrogen plants.

SHORT RESIDUAL: The residual oil obtained after neutral oils have been removed by distillation.

SKIMMING: Distillation of crude oil to remove light fractions only.

SLACK WAX: Crude wax obtained by pressing paraffin distillates.

SLOPS OIL: Mixture of oils lost and recovered in the refining process.

SLUDGE: Degradation residue obtained when treating petroleum.

SMOKE POINT: An index of diesel and kerosene fuels which measures smoking tendency when burned.

SOLVENT NAPHTHA: See Stoddard Solvent.

SOUR: Containing sulfur compounds such as hydrogen sulfide, mercaptans, as in sour gas or sour crude.

SPINDLE OIL: A grade of lube oil.

SPRAY OIL: A grade of oil used as a pesticide.

STABILITY: Resistance to change, generally refers to oxidation resistance of gasoline, other products in storage.

STABILIZER: A distillation process which removes light ends, generally butanes, from naphthas.

STILL: A distillation tower.

STODDARD SOLVENT: A naphtha used in dry cleaning or as a general solvent.

STRAIGHT RUN: Products directly obtained from distillation of crude oil before undergoing chemical change, such as cracking.

STRIPPING: The removal of volative products by heating.

SWEATING: A process in which oil is removed from wax by heating.

SWEET: Containing little sulfur or sulfur compounds, such as hydrogen sulfides and mercaptans.

T

TEL: Tetraethyl lead.

TAIL GAS: Sulfurous gases unreacted in sulfur recovery process.

TAR: Highly viscous polymerized residue produced in vacuum distillation, cracking coils. By-product of the cracking process.

TEMPERING OIL: Neutral oils.

THERMAL CRACKING: See Cracking.

THERMAL REFORMING: See Reforming.

THIEF: A device for taking samples of petroleum from specific location in the tank.

TOLUENE: An aromatic hydrocarbon derived from crude oil.

TOPPED CRUDE: Residual crude oil obtained in topping plant.

TOPPING: See Skimming.

TOWER: A vertical vessel in which petroleum is distilled, or gases are absorbed, etc.

TREATING: A process in which petroleum is contacted with chemicals to improve product quality.

TURNAROUND: A maintenance operation in which a refinery or process unit is shut down and repaired.

U, V

VACUUM DISTILLATION: Separation of crude oil by distillation below atmospheric pressure.

VAPOR PRESSURE: Pressure exerted by a liquid at a given temperature in a closed vessel in the absence of air or other compounds.

VAPOR RECOVERY: A system used to collect hydrocarbon vapors from vents and relief devices for reuse in the refinery.

VIRGIN STOCK: See Straight Run.

VISBREAKING: A process of mild thermal cracking in which oil viscosity is reduced.

VISCOSITY: A measure of resistance to flow, often determined by the time for liquid to pass through standard orifice.

W

WATER WHITE: A grade of oil color.

WAX DISTILLATE: A neutral oil containing recoverable paraffin wax.

WAX TAILING: Heavy tarlike distillate recovered in coking process.

WET GAS: Light hydrocarbon gas containing heavy hydrocarbons which are easily condensed.

WHITE OIL: A grade of colorless, light lube oil.

WILD GAS: Natural gasoline containing dissolved light ends.

X, Y, Z

XYLENE: An aromatic hydrocarbon derived from crude oil.

YELLOW SCALE: Low-grade paraffin wax.